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SCANNING AND TRANSMISSION ELECTRON MICROSCOPE STUDIES OF MACERALS AND PORE STRUCTURE IN COALS OF DIFFERENT RANK

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PREFACE

The intended purpose of this report was to evaluate the utility of scanning and transmission electron microscopy for studies of coal porosity, coal macerals and mineral-maceral relationships of coals. This work is significant as this is the first study of this type applied to coals of different rank. The contents of the report should be useful to those researchers concerned with the development of electron optic techniques that can usefully compliment standard coal petrographical analyses.

ABSTRACT

The objectives of the program were to develop, test and evaluate electron microscopy techniques for the study of coal macerals, coal minerals and pore structure of coals of different rank. Four coals: eastern high volatile bituminous, western low volatile bituminous, western medium volatile bituminous and a Saskatchewan lignite were selected for the study.

The scanning electron microscope (SEM) was used to observe maceral and mineral structure in whole coal samples. The utility of the SEM for studying coal macerals was determined by comparing electron micrographs with optical micrographs of identical areas. The energy dispersive X-ray analyzer (EDXA) was used to study mineral-maceral relationships for a particular coal type.

Replicated and ion milled coal samples were examined using the transmission electron microscope (TEM). This phase of the study evaluated sample preparation techniques that would allow for the observation of coal porosity in particular macerals.

It was determined that the SEM is of limited utility for the study of coal maceral structure. However, the SEM/EDXA if used in concert with an optical microscope has the capability of identifying mineral-maceral relationships for a particular coal. The TEM study suggested that both ion milling and replication techniques are suitable for the observation of coal porosity.

The project is significant as it has identified new areas of coal research to which the SEM and TEM could be applied.

EXECUTIVE SUMMARY

The purpose of this study was to determine the capability of the scanning electron microscope (SEM) and transmission electron microscope (TEM) with regard to extending the information obtained from standard coal petrographic analyses. In particular, the utility of the scanning and transmission electron microscopes for studying coal macerals, coal porosity and mineral-maceral relationships was to be evaluated.

It was determined that improved image contrast of macerals could not be achieved in either the secondary electron or backscattered modes of the SEM. This was attributed to the similarity in chemical composition between different macerals, regardless of coal rank. This similarity in the organic matrix of coals implies that the number of secondary or backscattered electrons originating from a coal surface is not sensitive to changes in coal rank or maceral type. Thus, the SEM has limited applicability for maceral characterization.

However, it was discovered that if the energy dispersive X-ray analysis (EDXA) ability of the SEM was used in concert with an optical microscope, mineral-maceral relationships could be detected. Maceral characterization (using standard coal petrographic methods) was performed with the aid of a high powered optical microscope. The mineral phases of these areas were then characterized using the SEM/EDXA. The results of these studies suggest that this method could be extended to develop mineral-maceral relationships for coals of different rank. This is very important with regard to the efficiency of coal conversion technologies that are influenced by the potential catalytic activity of mineral phases. It is important to note that more work is required to fully evaluate the method.

The TEM studies focussed on attempting to detect coal porosity in maceral groups. The success of this study was dependent on the method of sample preparation. Two methods were tested and evaluated: replication of coal surfaces and production of thin coal samples by ion milling. Ion milling of coal samples allowed for the visualization of both random and interconnected pores. The replication method was demonstrated to have potential with regard to observing pore populations in maceral groups. Documentation of pore features is important as pore size and the extent of linking between pores influences coal porosity and permeability which are important to coal conversion processes. It also must be noted that this limited study of coal porosity did not provide sufficient data with which to objectively evaluate the replication and ion milling techniques. More research is required to fully develop TEM techniques important to coal conversion technology.

In summary, this study has indicated that if sufficient effort was applied the SEM/EDXA could be used to develop mineral-maceral relationships for a particular coal type while pore characterization may be studied using the TEM. Knowledge of mineral-maceral relationships and pore characteristics may be potentially useful to the evaluation of coal utilization processes such as combustion, liquefaction and gasification.

1. INTRODUCTION

Coal is an important source of energy. Canada, by its geological nature has an abundant supply of coal estimated at 1.4×10^{11} tonnes in total. The shift towards the utilization of coal as an energy source is a logical and necessary step for the future. Efficient utilization of coal requires characterization of the mineral and maceral components and an understanding of how these components influence coal conversion processes. In particular, further research and development is required to document coal characteristics, such as size and spatial distribution of pores, identification of submicron minerals particles determination of maceral-mineral relationships and the microstructure of macerals. It is also important to note that the dependence of these characteristics on coal rank is critical to the development of a more complete understanding of the chemical and physical factors crucial to coal conversion processes.

The scanning electron microscope (SEM) and transmission electron microscope (TEM) have proven useful for characterizing coal and coal processes, but these studies have generally been limited to coals of one rank. Thus, more research and development is required to determine the scope of electron optical methods for studying and evaluating coal and coal conversion processes.

2. OBJECTIVES

The objectives of the program were to develop, test and evaluate electron microscopy techniques for the study of coal macerals, coal minerals and pore structure of coals of different rank. Four coals: eastern high volatile bituminous, western low volatile bituminous, western medium volatile bituminous and a Saskatchewan lignite were selected for the study.

As well a literature survey of the present status of electron

microscopy methods for coal characterization was conducted. The literature review is found in Appendix A of this report.

3. PROCEDURE

3.1 Sample Preparation

This section of the report will describe the various sample preparation methods used to prepare coal samples for examination by electron microscopy.

3.1.1 Preparation of Coal Samples For Optical and Scanning Electron Microscopy Studies

For each coal type, crushed coal pellets were prepared and polished using method ASTM D2797-72 of the American Society for Testing and Materials. The method was followed exactly, except that a riffle sampler was not available for grinding of the coal. Consequently, all coals were ground in a standard mortar and pestle. Particles of the required size (850 μm) were obtained by passing the finely ground coal through a No. 20 sieve. Coal samples obtained in this manner were used to prepare crushed coal pellets.

Samples were also prepared that consisted of whole pieces of coal mounted within an epoxy binder. The reason for preparing whole coal pellets was to provide samples in which the spatial relationships of macerals and minerals were preserved. A similar mounting technique was necessary for the whole coal samples, because it was not otherwise possible to prevent the coal from disintegrating during polishing and subsequent handling. Every attempt was made to prepare whole coal samples that consisted of at least one maceral-maceral boundary, thus

maximizing the probability of observing the same maceral groups in both the SEM and the optical microscope.

These whole coal samples were prepared in the following manner. A suitable whole coal sample was selected and the surface to be observed was ground flat with Number 55 silicon carbide paper. The shape and volume of the sample was not considered important as long as it would fit within the diameter of the phenolic ring forms used to hold the coal in the epoxy resin. These phenolic ring forms (Buehler Ltd.) were 1.9 cm high with a diameter of 2.5 cm. Coal samples were generally selected such that the area potentially available for observation occupied as much of the phenolic ring area as possible. The phenolic rings were placed on a taped surface and sufficient epoxy resin (Armstrong epoxy resin C-4 with activator D, Armstrong Products Co. and Helix Bonding Agent R-283 with Hardener B., Carl H. Biggs Co. Inc.) was added such that the surface of the coal and epoxy was level with the top of the ring. The epoxy resin was then allowed to harden at ambient room conditions for 24 hours. After this time the coal surface was prepared using a sequence of silicon carbide grits (120 to 600), followed by alumina polishing (1.5 μm to 0.5μm). A high speed wheel was used for all stages of the polishing except for the final alumina polishing, which was done carefully by hand. The high speed wheel also had the facility for wet polishing of coal samples. The coals, except in the case of Saskatchewan lignite, were wet-polished. It was necessary for the lignite to be dry-polished because exposure to moisture caused cracking of the surfaces of this particular variety.

After polishing, the crushed and the whole coal pellets could then be viewed using the reflectance mode in an optical microscope. It is important to note that as oil-

immersion reflected light objectives were not available, all optical work was performed using air objectives. The ASA setting of the cameras (35 mm and polaroid) was varied to maximize contrast. To obtain suitable images using the SEM, the samples were coated with a thin vacuum-evaporated film of carbon (10 nm). If required, this carbon film could be removed by minimal re-polishing of the sample surface with fine alumina.

3.1.2 Preparation of Coal Samples For Transmission Electron Microscopy Studies

Coal samples for transmission electron microscopy studies were prepared using either ion milling or replication techniques.

3.1.2.1 Preparation of Coal Replicas For Transmission Electron Microscopy Studies

Samples of coal selected for replication were mounted in phenolic rings, using epoxy binder (as described in section 3.1.1). The surface was then polished to the same degree as required for coal petrographic studies in reflected light. Areas for replication were chosen using an optical microscope in the reflectance mode. These areas were recorded photographically. An attempt was made to select areas comprising at least two maceral types. As replication is a method that requires the surface to have some relief, the coal samples were etched using chromic acid or plasma etching. In both procedures, the coal was etched for no more than one minute. It was assumed that these etching techniques would preferentially etch one maceral

type over another. Thus, the required relief would be produced.

To form the replicas, thin replicating tape (0.022 mm) made of cellulose acetate was used (Ernest Fullam Inc.). This was first softened by a brief immersion in acetone and then carefully applied to the surface to be replicated. After hardening for approximately 10 minutes, the tape was carefully removed from the coal surface. The replica side of the tape was then carbon coated using a vacuum evaporator. A piece of the replica approximately 3 sq. mm was cut out and placed carbon side up on a 3.0 mm diameter copper grid. The grid plus replica were placed on an acetone Jaffe washer for one hour. This procedure softened the cellulose acetate tape. The tape was then completely dissolved away by placing the grid and replica in an acetone condensation washer. This procedure yielded a carbon replica of the coal surface, supported on a copper grid.

3.1.2.2 Preparation of Ion Milled Coal Samples For Transmission Electron Microscopy Studies

Coal samples to be ion milled were selected using an optical microscope (reflectance mode). Selected samples were fastened to a glass microscope slide using Canadian Balsam. The coal was first ground to a thickness of approximately 0.1 mm using standard polishing methods. The coal sample was then removed from the glass slide by dissolving the Canadian Balsam in alcohol. A section of

the coal wafer, less than 6 sq. mm was inserted into a copper ring (1 mm i.d.). A fast setting polyvinyl alcohol glue was used to attach the coal specimen to the ring. The prepared coal sample was then thinned using an ion beam milling apparatus (Edwards High Vacuum, model IBT 200). The sample stage was modified so that the coal could be cooled during the ion thinning. The system was normally operated at a 6 kV accelerating voltage with a 20 - 30 μA specimen current. Specimens were initially tilted at 25° to the beam. This angle was reduced to 10° - 15° as the ion milling proceeded.

3.2 Microscope Description

3.2.1 Scanning Electron Microscope

The SEM used in these studies was a SEMCO Nanolab 7 equipped with a Kevex 7000 energy dispersive x-ray microanalyzer. Coal samples were examined with a 30 kV accelerating voltage and with a sample tilt of 10°.

3.2.2 Transmission Electron Microscope

Two transmission electron microscopes were used for these studies. One microscope was a Philips EM400T TEM equipped with a scanning transmission microscope accessory, an EDAX PV 9100/60 energy dispersive X-ray microanalyzer and selected area electron diffraction capability. The other microscope was a Philips EM301S TEM equipped with a Kevex 5100 energy dispersive X-ray microanalyzer and was also capable of selected area electron diffraction. The

Philips EM400T and EM301S microscopes were operated at 100 and 80 kV accelerating voltages respectively.

3.2.3 Optical Reflectance Microscope

A Zeiss Universal Research polarized light microscope equipped with a voltage stabilized photometer was used to perform reflectance studies of coal surfaces. These studies were performed using a light filter with a wavelength of 546 nm. The linearity of the photomultiplier system was checked using a series of neutral density filters. All reflectance data were collected using dry objectives.

3.3 Photographic Materials

Optical microscope images were recorded using 35 mm Kodak Technical PAN 2415 (TP135-36) or Polaroid Type 55 P/N film. Scanning electron microscopy images were recorded using Polaroid Type 55 P/N film. Transmission electron microscopy images were recorded on Kodak electron image plates (3-1/4" x 4").

3.4 Low Temperature Asher

A Plasmod plasma asher was used to etch coal surfaces. The plasma asher was run at 18 - 20 watts with an oxygen pressure of 1.0 Torr.

3.5 Reflectance Measurements of Coal Surfaces

Coal samples were prepared according to the method outlined in section 3.1 of this report. Mean maximum reflectance of selected macerals was measured in accordance with ASTM method D2798. Unfortunately, due to unavailability of an oil immersion objective, all optical and reflectance data were collected using dry

objectives. The relative reflectance of macerals within a field of view was used to determine maceral identity.

3.6 General Procedure For Scanning Electron Microscopy Studies of Coal Macerals

Coal samples were prepared as described previously. An area of interest was located using the optical microscope and the mean maximum reflectance of various macerals measured.

This area was then marked, in order that it could be easily relocated during the SEM study. Maceral images were also recorded photographically. As oil immersion objectives were not available, the contrast quality of the micrographs was limited to that obtainable in air. Thus the ASA setting of the microscope camera was varied to maximize maceral contrast. The sample was then carbon-coated and the equivalent area viewed in the scanning electron microscope at a magnification equivalent to that used to record optical images. Every effort was made to maximize contrast of the images so that the capability of the SEM to produce maceral images could be viewed. The secondary electron, backscattered electron, and energy dispersive X-ray analysis capabilities of the SEM were all utilized.

It was discovered that the backscattered image produced by the SEM was not suitable for these studies. Although this mode is extremely useful for detection of minerals it is of very limited utility for examination of macerals. This is due to the fact that the distribution of carbon, hydrogen, oxygen and sulphur in macerals of coals of different rank is not sufficiently ient variable for the backscattered mode to be useful.

Backscattered images were examined for all coal specimens. However, these images were not recorded unless an unusual feature was observed. Thus, all SEM work reported was performed

using the secondary electron mode.

3.7 Coal Samples Provided For the Electron Microscopy Study

Coal samples for this study were provided by the Department of Energy, Mines and Resources. These included eastern high volatile bituminous, western medium volatile bituminous, western low volatile bituminous, and Saskatchewan lignite coals. In addition, two finely ground bituminous and sub-bituminous oxidized coals were provided.

3.8 Method of Maceral and Mineral Characterization

Maceral groups were identified by comparing maceral detail with documented examples of known maceral types illustrated in Stach's Textbook of Coal Petrology (Third Revised and Enlarged Edition, Gebruder Borntraeger, Berlin, Stuttgart 1982). Mean maximum reflectance data were also collected for the maceral groups viewed on a particular coal surface. Although the numerical results of these studies are not reported, the variation in relative reflectances was used to distinguish between the vitrinite, inertinite and exinite maceral groups.

It is important to note that it was not always possible to distinguish clearly between fusinite and semi-fusinite. Thus, whenever the assignment was ambiguous, the maceral group was reported as semi-fusinite/fusinite.

Elements attributable to mineral phases were identified using energy dispersive X-ray analysis. The identity of mineral phases present in a maceral group was thus determined from the relative amounts and types of elements present. It is realized that this technique is not completely definitive, and therefore mineral

assignments may be subject to error.

4. RESULTS

4.1 Optical and Scanning Electron Microscopy Studies of Coal Macerals

A scanning electron microscopy study of four coals, of different rank, was performed in order to determine the utility of the SEM with regard to maceral and mineral characterization. The four coal types used in the study are described in Table 1. These coals and their maceral analyses were provided by the CANMET Energy Research Laboratories. Results for the scanning electron and optical microscopy studies of each coal will be discussed separately.

It is important to note that crushed coal pellets were not particularly useful for this study. In particular, it was not always possible to distinguish in the SEM image, between the various macerals and the epoxy binder. Thus, it was very difficult to obtain a meaningful image in the scanning electron microscope. Consequently, whole coal samples were used for the entire study described in the following section.

4.1.1 Optical and Scanning Electron Microscopy Studies of A Western Low Volatile Bituminous Coal

The data of Table 1 indicate that the maceral content of the western low volatile bituminous coal is composed primarily of vitrinite, fusinite and semi-fusinite. Macerals were identified using maceral reflectance, maceral composition (as provided by CANMET), and comparison with known maceral images such as those contained

in Stach's Textbook of Coal Petrology.

Figures 1 to 18 include scanning electron and optical micrographs as well as EDXA spectra of selected maceral groups from a western low volatile bituminous coal.

This coal type has a high content (approximately 45%) of fusinite and semi-fusinite. Thus, many of these micrographs contain images of these maceral groups.

Figure 1 is an optical micrograph of what is obviously fusinite showing 'bogen' structure. The area of lesser intensity is probably vitrinite. The very dark areas are mineral clusters. The scanning electron micrograph (figure 2) taken at equivalent magnification does not show any of the fusinite structure. Indeed the maceral content is featureless and appears as an inhomogeneous body. The lighter areas of Figure 2 are mineral phases. EDXA analyses of the mineral content are presented in Figures 3 and 4. These spectra suggest the presence of the mineral types such as pyrite, pyrrhotite, calcium sulphate and clay minerals. The detection of phosphorous (figure 3,) also suggests the presence of a mineral such as apatite, $9CaO.3P_2O_5.CaF_2$.

Figures 5 and 6 are optical and SEM micrographs of another area from the western low volatile bituminous coal. The optical micrograph shows the presence of the fractured cell walls of fusinite. A distinctive boundary between the fusinite and another maceral group, most probably vitrinite, is clearly visible. The SEM micrograph of these macerals fails to distinguish the collapsed cellular structure of the fusinite. Indeed, all the organic matrix of this coal area is featureless in the SEM image. However, it is interesting to note that the fusinite

contains larger quantities of mineral phases than the vitrinite. Energy dispersive X-ray analyses of these two areas, shown in figure 7, indicate the presence of the elements aluminum, silicon and sulphur. Due to the absence of calcium, iron and barium, the sulphur may be attributed to the organic matrix. The silicon and alumina suggest the presence of clays and perhaps quartz.

Figure 8 is an optical micrograph of another area of polished western low volatile bituminous coal. The top portion in the micrograph is considered to be semi-fusinite with the other maceral area assigned to vitrinite. The original cell structure of the semi-fusinite has been degraded. The scanning electron micrograph (figure 9) clearly distinguished the semi-fusinite from the vitrinite. However this is largely due to the presence of the cellular structure which enhances the morphology of the surface.
In the secondary electron image of polished coal surfaces minerals generally appear as lighter phases. Thus, this SEM micrograph suggests a reduced mineral content in this coal sample. Energy dispersive X-ray spectra for the two maceral areas are presented in figures 10 and 11. Figure 10 indicates the presence of silicon, aluminum and sulphur in the semi-fusinite. Figure 11 suggests that the same species are present in the vitrinite but in lesser quantities. However, the vitrinite would seem to contain more organic sulphur than the semi-fusinite. Little inorganic sulphur is present in these two macerals. As this normally requires that the sulphur is associated with elements such as barium, calcium or iron. Due to the intensity of the silicon and aluminum lines in the spectrum of the semi-fusinite, it would appear that this maceral contains more mineral-bearing elements than vitrinite. It is reasonable to

conclude that clays and some quartz are present in this coal sample.

Figure 12 and 13 are optical and scanning electron micrographs of semi-fusinite and vitrinite of a western low volatile bituminous coal. As was indicated for the previous data, the SEM was not able to distinguish between the two maceral types. The SEM micrograph does, however, clearly indicate that the mineral phases are concentrated in the semi-fusinite. Energy dispersive X-ray analyses indicate the presence of the elements, aluminum, silicon, sulphur and iron. The presence of iron and calcium is consistent with some pyrite, pyrrhotite and calcium sulphate, embedded largely in the semi-fusinite. The observed silicon and aluminum may be attributed to varying amounts of clay minerals.

Figures 15 to 18 contain optical, scanning electron and energy dispersive X-ray data for a final sample of the western low valatile bituminous coal. The maceral identity of the bright area of the optical micrograph is difficult to assign. In addition, the scanning electron micrograph (figure 16) presents this area in sharp contrast to the other adjoining area. The energy dispersive X-ray spectra of this adjoining area (figure 17) indicates the presence of only iron, calcium and manganese probably in the form of the oxides or carbonates. Indeed, it is suspected that this area is largely composed of such mineral phases and very little organic matter. The comp-

aratively bright area of the optical micrograph and corresponding dark area of the SEM micrograph is largely an organic matrix. The energy dispersive X-ray spectrum (figure 18) indicates the presence of elements such as silicon, aluminum, phosphorous, sulphur, calcium and iron. This is consistent with mineral phases such as quartz, clays, pyrite, pyrrhotite and apatite. The organic matrix also probably contains carbon bound sulphur. This maceral group is assigned to vitrinite. This assignment was based primarily on reflectance data and also due to the fact that this area does not resemble fusinite, semi-fusinite or resinite.

4.1.2 Optical and Scanning Electron Microscopy Studies of A Western Medium Volatile Bituminous Coal

The data of Table 1 indicates that this particular coal is composed primarily of vitrinite, and semi-fusinite with small amounts of fusinite and micrinite. Figure 19 is an optical micrograph of a polished area of western medium volatile coal. The top maceral group is thought to be semi-fusinite, the bottom area is epoxy binder. The dark areas, which appear brightly in the SEM micrograph (figure 20) are minerals. Energy dispersive X-ray analyses of the semi-fusinite (figure 21) indicates the elemental distribution for this area. The elements found in the semi-fusinite were aluminum, silicon, phosphorous, sulphur and calcium. The relative levels of phosphorous and calcium are comparatively greater than the levels of the other elements present. This is consistent with significant quantities of apatite, $9CaO.3P_2O_5.CaF_2$, contained in the semi-fusinite.

The aluminum and silicon may be attributed to quartz or clay minerals. The sulphur may be present as calcium

sulphate and organic sulphur. Unfortunately it was not possible to determine the relative quantities of these sulphur sources.

Figure 22 is an optical micrograph of another area of western medium volatile coal. The micrograph clearly shows a boundary between two maceral groups that are

assigned to semi-fusinite and vitrinite. The scanning electron micrograph (figure 23) distinguishes the semi-fusinite from the vitrinite. However, this may be attributed to differences in topography between the two macerals. Energy dispersive X-ray analyses of these semi-fusinite and vitrinite macerals are presented in figure 24 and 25 respectively. These spectra suggest the following:

(i) the semi-fusinite contains the mineral apatite, $9CaO \cdot 3P_2O_5 \cdot CaF_2$;

(ii) the semi-fusinite contains a small amount of pyrite;

(iii) organically-bound sulphur is more often detected in vitrinite rather than semi-fusinite;

(iv) both macerals contain mineral phases composed of aluminum and silicon.

The optical micrograph of figure 26 illustrates a wedge-shaped semi-fusinite maceral surrounded by vitrinite. The platelet-like features beneath the wedge may be compressed intercellular spaces of fusinite. None of the maceral features is visible in the scanning electron micrographs of the same area. However, the scanning electron micrograph (figure 27) clearly indicates the minerals are pre-

dominantly distributed within the semi-fusinite. The energy dispersive X-ray spectrum of figure 28 is consistent with the same mineral types present as was observed for the semi-fusinite maceral in other examples of western medium volatile bituminous coal. The vitrinite contained lesser amounts of these minerals and had a higher level of sulphur than the semi-fusinite, (figure 29). In particular, the peak heights for calcium and sulphur are similar for the minerals of the vitrinite maceral, whereas for semi-fusinite, they were significantly different. (the peak height for calcium is much greater than that for sulphur). However, the peak height ratio of calcium to phosphorous is approximately the same in both spectra. Thus it is likely that the vitrinite contains some organic sulphur.

Figure 30 is an optical micrograph composed of dark cells of fusinite and vitrinite in a western medium volatile bituminous coal. The companion scanning electron micrograph (figure 31) does not distinguish the boundary between the two organic matrices. It does show that the fusinite cells are filled with a mineral phase. Energy dispersive X-ray analysis of this mineral phase indicated that the elements, silicon, aluminum and sulphur were present. The silicon and aluminum must correspond to mineral phases such as quartz and clay minerals. In the absence of calcium, barium and iron, the sulphur is probably organic in origin.

The energy dispersive X-ray spectrum (figure 33) was consistent with the vitrinite containing lesser amounts of these mineral phases.

4.1.3 Optical and Scanning Electron Microscopy Studies of An Eastern High Volatile Bituminous Coal

The eastern high volatile bituminous coal provided for the study contains approximately 78 per cent vitrinite with the balance of the macerals being fusinite, semi-fusinite, exinite/resinite and micrinite.

Figure 34 is an optical micrograph of a polished area viewed in reflected light. Three maceral groups: vitrinite, fusinite/semi-fusinite and exinite are present. The location of the vitrinite and semi-fusinite/fusinite are indicated in figure 34. It should be noted that it was not considered possible to distinguish the fusinite from the semi-fusinite. The exinite can be recognized as the various lens shaped dark areas. Careful examination of the scanning electron micrograph (figure 35) indicates that sufficient contrast is present to distinguish the maceral groups. Energy dispersive X-ray analyses of these maceral areas produced virtually identical spectra. Figure 36 is a representative spectrum of this survey. This spectrum implies the following:

(i) due to the low intensities of the iron and calcium peaks in relation to the sulphur peaks, most of the sulphur must be present as organic sulphur with some pyrite and calcium sulphate;

(ii) as no aluminum, but some silicon is present, the other mineral phase is most probably quartz.

Figures 37 to 40 present optical microscopy, scanning electron microscopy and energy dispersive X-ray analysis data for another polished surface of eastern high volatile bituminous coal. The optical micrograph (figure 37) depicts exinite lenses distributed within a vitrinite maceral. The bottom of the micrograph also has some

semi-fusinite/fusinite present. As with the previously discussed samples, the exinite is visible in the scanning electron micrograph (figure 38). Energy dispersive X-ray analysis of the mineral cluster (figure 39) identifies the mineral phases as iron sulphides, calcium sulphate and clays or quartz. Figure 40 is an EDXA spectrum of an area with no visible mineral content. The strong sulphur peak identifies organic sulphur.

The data collected from the microscopic observation of another sample of eastern high volatile bituminous coal is presented in figures 41 to 44. Figure 41 is an optical micrograph containing examples of what appears to be vitrinite, semi-fusinite/fusinite and exinite. In particular, the relative intensity of the reflected light from these areas corresponds well to that reported for these macerals. The maceral assignments within the photograph are questionable. This is due to the fact that significant quantities of exinite and semi-fusinite/fusinite appear to be present. This observation contradicts the maceral analyses provided by CANMET. In this analysis, vitrinite is the major maceral present with very little of the other macerals present. However, it must be noted that the very small area of the optical and SEM micrographs need not represent the total maceral analysis for a coal type. Thus, the large band in the centre of the photograph is probably in-situ fusinite or semi-fusinite. The scanning electron micrograph (figure 42) does not distinguish any of the maceral areas. It does however suggest that minerals are associated with the central band. The energy dispersive X-ray analysis of this area (figure 43) indicates the presence of pyrite, silicon and aluminum. An EDXA spectrum of the area below this band (figure 44) indicated the presence of iron sulphides, perhaps some calcium sulphate and organic sulphur.

The data of figures 45 to 48 are similar to that just discussed previously. The bright band pictured in the optical micrograph (figure 45) has the same EDXA spectrum, (figure 47) as the similarly bright band in figure 41. This is the same material, probably fisinite or semi-fusinite. The darker area is vitrinite or exinite (it was not possible to clearly distinguish between the two macerals). The scanning electron micrograph does not readily distinguish maceral boundaries but does show a strong mineral concentration within the semi-fusinite/ fusinite maceral.

4.1.4 Optical and Scanning Electron Microscopy Studies of Lignite

The Saskatchewan lignite provided for this study proved to be incompatible with both optical and scanning electron microscopy studies. Figure 49 is an optical micrograph that is representative of all lignite surfaces examined. This micrograph contains spore-like masses within a layered structure. The equivalent area is depicted in a scanning electron micrograph, (figure 50). The micrograph is of low quality but does indicate the presence of the spore-like material. The low quality is principally due to the charging effect that results from insufficient carbon being deposited in the area adjacent to these spores. The SEM micrograph is otherwise featureless. In general, energy dispersive X-ray analysis of this coal, regardless of the area examined, yielded a spectrum similar to that of figure 51. The spectrum indicates that the lignite must contain pyrite or pyrrhotite and calcium sulphate. The aluminum is probably due to alumina polishing powder that lodged in the many crevices of the lignite surface.

4.2 Transmission Electron Microscopy Studies of Coals

4.2.1 Transmission Electron Microscopy Studies of Ion Milled Coals

The purpose of the transmission electron microscopy study of thin coal sections produced by ion milling was to evaluate the utility of the method for observing the microstructure of coal. To accomplish this, the samples of eastern high volatile bituminous, western medium volatile bituminous, western low volatile bituminous, Saskatchewan lignite and two partially oxidized bituminous and sub-bituminous coals were ion milled.

In general, all coals were extremely resistant to ion milling and a period of approximately two weeks was required to produce a coal sample sufficiently thin for examination. Consequently only one thinned sample was prepared for each coal type. As only a limited number of samples could be ion milled, the method could not be fairly evaluated. However, the exercise did allow for a partial evaluation of the technique.

Figures 52 and 53 are transmission electron micrographs, of a thin section of ion milled eastern high volatile bituminous coal. The micrographs show pores in the coal matrix. The particles in the pores may have some significance with regard to pore formation. The size of the pores ranges from 30 nm to 50 nm. The pores appear to be interconnected to some extent. It is not possible to determine with which maceral group these pores reside. However it has been observed by Harris and Yust (Bibliography reference 7) that porosity in high volatile bituminous coals resides within vitrinite and inertinite.

Thus, these pores may reside within a vitrinite maceral as there is little inertinite in this coal type.

Figures 54 and 55 are transmission electron micrographs of thinned western medium volatile bituminous coal. Figure 54 indicates the presence of pores in the left side of the photograph. Figure 55 is a higher magnification of this area. These pores are approximately 15 nm to 30 nm in size and are interconnected. Again it is not possible to say with any certainty the maceral group with which they are associated. However, the upper part of the photograph contains images of a granular material similar to that observed by Harris and Yust. These researchers (reference 7) assigned this granular material to micrinite. As micrinite is associated with exinite, the pores may be contained within this maceral group.

The western low volatile bituminous coal proved very difficult to ion mill. Figure 56 shows a thin piece of this coal (magnification 22,000) covered with a large number of globules. Energy dispersive X-ray analysis of these globules indicated that they were mainly composed of copper. The copper is from the copper mounting ring which actually ion milled at a faster rate than the coal, and eventually had to be replaced. Ion milling of this coal type also resulted in the formations of "ripples", (figure 57). These "ripples" have been reported by other researchers and are not considered to be coal maceral features. Rather, they are a result of the beam interacting with the coal. Figure 58 is a very high magnification (98,000x) of a thin section of western low volatile bituminous coal. This section is not influenced by artifacts such as copper residue or "rippling effects". A number of "spots" are visible. These spots may be pores, however it is realized that this is largely

speculative. Pore channels are not visible and if these are pores, they are in the 10 nm to 20 nm range.

Two partially oxidized coals were provided by CANMET. Samples of ground bituminous and sub-bituminous coals that had been heated to 150°C were mounted in epoxy binder and ion milled. Both of these samples were examined using the SEM energy dispersive X-ray analyzer. Figures 59 and 60 indicate that the sub-bituminous coal had been ground to a finer size than the bituminous. In addition, the heated bituminous coal probably contains clays, calcium sulphate, iron sulphide and organic sulphur, as illustrated by the EDXA spectrum in figure 61. The sub-bituminous heated coal had a similar EDXA spectrum, but contained signficantly less sulphur (figure 62). The calcium and iron may therefore be present as oxides or carbonates. Figure 63 is a typical transmission electron micrograph representative of the results obtained from ion milling a thin section of epoxy-mounted bituminous or sub-bituminous coal. It is difficult to determine accurately if epoxy binder or heated coal particles are being observed. This is due to the fact that both of these materials are chemically similar. Attempts were made to locate maceral or pore structure but definite assignments could not be made. It may have been more useful if particular maceral groups were first identified in whole coal samples, then heated and subjected to TEM analyses.

The Saskatchewan lignite provided for this study also could not be ion milled without first increasing the mechanical strength of a sample. This was accomplished by embedding ground lignite (-20 mesh) into epoxy binder. The sample could then be ground down to a thickness suitable for ion milling. Ion milling of this coal type with

subsequent examination by the TEM produced surfaces containing "ripples". These ripples were most likely produced by the ion beam and are clearly visible in figure 64.

4.2.2 Transmission Electron Microscopy Studies of Coal Replicas

From the previous section it is obvious that the ion milling of coals to produce samples suitable for TEM analysis is a "hit or miss" method. To enhance the chances of detection of observing maceral microstructures or pore structure, a replication method was used. A reflected light micrograph of a particular maceral was first obtained followed by replication of the area as described in section 3.1.2.1. To obtain the necessary relief for replication, samples were lightly etched in chromic acid or in an oxygen plasma.

Use of chromic acid to produce coal surfaces suitable for replication was not an acceptable method. Figures 65 to 68 are scanning electron micrographs of samples of eastern high volatile bituminous coal that had been etched for 90 seconds followed by replication. These micrographs indicate that use of chromic acid results in a severely etched surface not suitable for replication. Replication of these chromic acid etched surfaces also removed large quantities of coal and mineral matter with the replica.

Fortunately, plasma etching is comparatively less destructive. Figure 69 is scanning electron micrograph of a plasma etched eastern high volatile bituminous coal. After 60 sconds, sufficient relief has been produced for replication of the coal surface. Large cracks etc. have not been introduced. It is noted however that craters are

present on the surface. Presumably some minerals have been dislodged by the etching process.

Figure 70 suggests that during plasma etching mineral particles may overheat and gasify coal. Thus, for high mineral content coals, the intensity of the etching process should be reduced.

Replication was attempted of all four coals provided by CANMET. The Saskatchewan lignite would not produce suitable replicas. The surface of this coal was difficult to polish and upon etching, regardless of method, severe fracturing occurred. Thus, the features of any replica were seriously distorted by this fracturing.

Some success was achieved with the western low volatile bituminous, western medium volatile bituminous and eastern high volatile bituminous coals. As previously discussed, the surfaces of these coals were plasma etched before replication. It is also important to note that the primary goal of the replication study was to determine the usefulness of the method with regard to the detection of coal pores. To achieve meaningful data therefore, replicas were made of one maceral group that had been characterized using optical microscopy.

Figures 71 and 72 are optical micrographs of surface areas of a polished western medium volatile bituminous coal. Both of these micrographs indicate that the replicated area consisted mainly of semi-fusinite. Figures 73 and 74 are transmission electron micrographs of replicas produced from the coal surface in figure 71. Similarly figures 75 and 76 correspond to figure 72.

The transmission electron micrographs of the replicas,

figures 73 and 76, have features that may be assigned to coal porosity. The large crater-like areas are presumed to be due to the loss of minerals. If these smaller areas do represent pores, they are approximately 20 nm in diameter. It is also noted that these pore-like features are heavily concentrated in one particular area of the replica.

Figure 77 is an optical micrograph of a surface of western low volatile bituminous coal. The dark area of the micrograph contains mineral matter embedded in vitrinite, the lighter area is either fusinite or semi-fusinite. Figures 78, 79 and 80 are transmission electron micrographs of the replicas obtained from the semi-fusinite/fusinite. These replicas have many small circular features that may also be attributed to coal pores. As with the previous coal, these circular configurations have a diameter of 30 nm.

Finally, replicas of an eastern high volatile bituminous coal were also prepared. Figure 81 shows the optical micrograph of the area which was replicated. This area comprises the macerals, semi-fusinite/fusinite, vitrinite and exinite. As with the two other coals examined, features resembling pores are present in the transmission electron micrographs (figures 82 and 83). In particular, these pores seem to be restricted to the banded area of figures 82 and 83, and have approximate diameters of 20 - 30 nm. Due to the inhomogeneous distribution of macerals in the surface of coal (see figure 81), it is not possible to determine with which maceral group these pore-like features are associated. However, considering the magnification used to obtain figure 82, the banded area could be due to a spore or very narrow lens of exinite.

The probability of these replicated "pore-like" features being produced from coal pores will be more fully discussed in the next section.

5. DISCUSSION

5.1 Utility of Scanning Electron Microscopy for Examining Coal Macerals and Minerals

The purpose of these studies was to evaluate the usefulness of the SEM with regard to characterizing maceral and mineral phases of coal. It was also expected that an assessment would be possible as to the probability of identifying maceral-mineral relationships for particular coal types. The usefulness of the SEM with regard to maceral analysis will be considered first.

Useful images of macerals are difficult to obtain. The results of this study indicated that in most cases, sufficient contrast cannot be achieved to distinguish two maceral groups or even to examine maceral microstructure. Maceral detail, when observable, seems to be due to limited amounts of relief in the coal surface. This relief is introduced by such features as hollow cellular structures or differences in hardness between macerals. Relief introduced by hardness is produced during the polishing of the coal surface.

For example, figures 9 and 23 are scanning electron micrographs in which the semi-fusinite maceral is visible. However, this is due to the presence of cellular voids that contribute to the morphology of the coal surface.

An example in which relief produced from polishing improved the SEM image of coal macerals is provided in Figure 35. The corresponding optical image shows that this coal surface

is composed of semi-fusinite/fusinite, vitrinite and exinite. The exinite appears as dark lenses in the optical micrograph. These exinite lenses are also visible in the SEM micrograph because the exinite is raised slightly higher than the vitrinite. The semi-fusinite/fusinite is visible primarily due to its higher mineral content which enhances the contrast between it and the vitrinite.

Improved image contrast of macerals could not be achieved in either the secondary electron or backscattered modes of the SEM This is attributed to the similarity in chemical composition between different macerals, regardless of the rank of the coal. It is realized that the absolute amounts of carbon, hydrogen, oxygen and sulphur vary with coal rank; however, the differences are not sufficient for generation of image contrast in the SEM. That is, the macerals are primarily composed (70 - 80 per cent) of carbon with lesser amounts of other elements. This similarity in the organic matrix of coals implies that the number of secondary or backscattered electrons originating from a coal surface is not sensitive to changes in coal rank or maceral identity. Thus, the SEM has limited capability for maceral identification or characterization.

The results of this study are not completely negative. Experimental data were accumulated that were consistent with mineral phases being associated with one particular maceral type. This would imply that it is possible to establish coal mineral-maceral relationships. Such an exercise would involve documenting the maceral group optically, and then viewing the same area of the sample in the scanning electron microscope.

Data from the scanning electron microscopy study supports the above thesis. In particular, EDXA spectra of selected maceral

groups indicate the presence of different minerals and the distribution of these minerals between the groups. These data are summarized in Table 2. The bracketed numbers in the "elements determined by EDXA" column of Table 2 refer to the relative intensities of the X-ray lines on an arbitrary scale for particular elements. Except where indicated, the X-ray spectra were collected under identical instrumental conditions. Thus, it is possible to make meaningful comparisons between spectra collected from two maceral groups. It is realized that these data reflect a very limited study and the statements made in Table 2 do not strictly apply to a particular coal rank. Much more data would have to be collected in order to be specific. The data do, however, indicate that the EDXA analysis has the potential to distinguish differences in the quantity and quality of mineral phases between two macerals. On the basis of this limited survey it is reasonable to conclude the following:

(i) for eastern high volatile bituminous, western medium volatile bituminous and western low volatile bituminous coals, semi-fusinite/fusinite has a higher mineral content than vitrinite;

(ii) for all three coal types, vitrinite appears to have a larger quantity of organic sulphur than semi-fusinite/fusinite;

(iii) semi-fusinite/fusinite seems to contain the mineral apatite. This assignment is based on the observation of both calcium and phosphorous in the EDXA spectrum of this maceral.

To summarize, the optical and scanning electron microscopes may be used in concert to characterize mineral and maceral phases of a particular coal. Mineral-maceral relationships could be

developed if a statistically meaningful amount of data were collected.

5.2 Ion Milling as a Sample Preparation Method for Transmission Electron Microscopy Studies

Section 4.2.1 reported the results of an investigation of ion milling as a method for preparing coal samples for the TEM. The investigation was considered limited as sufficient time was available to ion mill only one sample of each of the four coal types and two oxidized coals provided for the study. The method can be very imprecise as it is difficult to determine the maceral identity of a particular ion milled section of coal. In addition, coal samples were noted to be subject to "rippling" caused by the ion beam. This effect was noticeable in ion milled samples of oxidized bituminous coal, Saskatchewan lignite and western low volatile bituminous coals. In one sample, ion milling was so slow that the copper mounting grid disintegrated, resulting in copper globules being dispersed over the coal samples.

During the early stages of this phase of the program, the ion milling apparatus was fitted with a liquid nitrogen cooled sample stage. The purpose of this was to prevent thermal degradation of the coals during ion bombardment. However, cooled coal samples proved to be remarkably resistant to ion milling. Thus, to increase the rate of thinning, ion milling was performed at room temperature. Visual inspection of ion milled samples with an optical microscope indicated that the coals did not degrade thermally.

Samples of eastern high volatile bituminous and western medium volatile bituminous coals were successfully ion milled.

Figures 52 to 55 are transmission electron micrographs depict-

ing pore structure in thin sections of eastern high volatile bituminous and western medium volatile bituminous coals. As described in section 4.2.1, the pores of the eastern high volatile bituminous coals range in size from 30 nm to 50 nm and are randomly distributed. In contrast, the pore structure of the western medium volatile bituminous coal are approximately 20 nm in diameter and are interconnected, thus indicating good permeability. It was suggested in section 4.1.2 that the pores of the western medium volatile coal are probably within an exinite maceral. Unfortunately, it was not possible to determine the maceral group to which the pores of the eastern high volatile bituminous belong.

To summarize, ion milling of coals can yield samples that are suitable for transmission electron microscopy studies. In particular, the method has excellent potential for studying pore structure in coals. It is not particularly useful for documenting maceral microstructure. This is because the ion beam always has the potential of producing artifacts that may be mistaken for maceral structure. Finally, micro-sampling techniques must be developed that will ensure selection of a known maceral type for ion milling. These techniques would be labour-intensive, but would result in the correlation of pore size and geometry with maceral groups for coals of different ranks.

5.3 Replication as a Sample Preparation Method For Transmission Electron Microscopy Studies

Section 4.2.2 describes the results of a replication study on eastern high volatile bituminous, western medium volatile bituminous and western low volatile coals. This technique was not useful for studying the Saskatchewan lignite coal. The main consideration for these studies was to determine the probability of these pore-like structures actually being produced from pores during replication. The study cannot definitely answer this

question. However the following observations are consistent with these features being representative of coal pores:

(i) the circular areas have appropriate diameters for pores;

(ii) the pore-like areas are restricted to certain areas of the replica; for example see figure 76. This would suggest that they are not artifacts introduced by the replication process, as this would introduce these pore-like areas over the entire replica surface. However, it is important to note that removal of the replication tape could produce pore-like features. This is possible if portions of the replication tape stick preferentially to one maceral group. As the tape is removed small diameters (20 - 50 nm) of the replica could remain stuck to the surface. As these small areas release, they could induce relief in the replica, similar to that produced by a coal pore;

(iii) these pore-like areas are not due to the removal of sub-micron mineral manner by the replication tape. If this were the case, the sub-micron mineral matter would become embedded in the carbon coating and thus clearly be visible in the TEM;

(iv) figure 84 illustrates a replica to which a piece of western low volatile bituminous coal is attached. The coal is sufficiently thin to reveal areas of high contrast, which may be attributed to coal pores. If these are pores, their diameters are approximately 30 nm to 50 nm. These areas, as discussed in an earlier part of this report, could also be micrinite grains. However, the grains are usually somewhat larger than 50 nm in diameter.

To prove that these features are coal pores, a thin section

(ion-milled) of the replicated coal area would have to be produced. Pores would have to be detected in this thin sample. This would require the development of the necessary micro-handling techniques to handle the coal examination.

5.4 Scanning and Transmission Electron Microscopy Studies of Pure Macerals

Pure separated macerals were to be used in this study and these materials were to be supplied by CANMET. The purpose of this phase of study was to document electron optical images (SEM and TEM) of pure macerals. These images would be particularly useful with regard to transmission electron microscopy studies for characterizing macerals in whole coal samples. Any pore structure associated with various maceral types could also be documented. However, CANMET was unable to supply pure macerals and thus this part of the study could not be conducted.

6. CONCLUSIONS

The following may be concluded from these studies:

(i) the SEM/EDXA, if used in concert with an optical microscope, has the potential for establishing mineral-maceral relationships. However, a statistically meaningful amount of data must be obtained. The study should also be supplemented by bulk characterization of the mineral types present in the coal;

(ii) both replication and ion-milling techniques should be used in studies of coal pore structure. Replication has the potential to identify coals/macerals containing pores. Ion milling of a suitable sample allows for direct observation of these pores. This is important for determining if the pores are random or interconnected,

and thus if the coal has any internal porosity. Neither of these techniques seems suitable for maceral micro-structure studies.

7. RECOMMENDATIONS

The principal thrust of these studies has been to evaluate the use of electron optical methods for the study of coals.

The scanning electron microscopy study suggested that it is possible to establish mineral-maceral relationships for bituminous coals. A review of the literature indicated that studies of this type have not been performed. Consideration should therefore be given to investigating mineral-maceral correlations for various coal types. As a statistically meaningful amount of data must be accumulated, an investigation of even one coal type would be labour intensive.

The transmission electron microscopy studies focused on the use of ion milling or replication techniques to observe coal porosity. Both replication and ion milling methods have the potential capability of detecting and visualizing the pores in a maceral group. Sufficient success has been achieved in this study to warrant further research into the use of the transmission electron microscope to study coal porosity. In particular, these techniques may prove very useful for understanding the importance of coal pores in coal conversion processes. However it is important to note that more effort must be devoted to the development of micro-manipulation techniques which will allow a particular maceral group to be studied by all of the various techniques.

TABLE 1

Maceral Analysis of Coals
For Electron Optic Studies

Coal Rank	Per Centage of Various Macerals				
	Vitrinite	Fusinite	Semi-Fusinite	Exinite & Resinite	Micrinite
Eastern High Volatile Bituminous	77.8	2.6	8.8	6.6	3.6
Western Medium Volatile Bituminous	68.4	4.1	23.5	Not Reported	1.6
Western Low Volatile Bituminous	42	12	33	<1	2
Saskatchewan Lignite	Maceral Analysis not available				

* Note: These maceral analyses were provided by the CANMET ENERGY RESEARCH LABORATORIES.

TABLE 2

Observed Mineral Distributions Between The Vitrinite and Semi-Fusinite/Fusinite Macerals

Coal	Data Source	Maceral	Elements Determined by EDXA*	Comments
WLVB	Fig. 8 - 11	Semi-fusinite/ fusinite	Al(7), Si(14), S(1)	Reduced mineral content in vitrinite. Vitrinite contains more organic sulphur than semi-fusinite/fusinite.
		Vitrinite	Al(1), Si(3), S(3)	
	Fig. 12 - 14	Semi-fusinite/ fusinite	Al(11), Si(14), S(1), Ca,(1), Fe(0.5)	Semi-fusinite/fusinite contains more mineral phases composed of aluminum and silicon than vitrinite.
		Vitrinite	Al(0.5), Si(1), S(1.5), Ca(0.5), Ti(0.5), Fe(<0.5)	
	Fig. 15 - 18	Semi-fusinite/ fusinite	Si(7), P(4), S(1.5), Ca(11), Fe(0.5), Al(1)	Vitrinite contains large quantities of oxides or carbonates or iron, calcium and manganese,semi-fusinite/ fusinite, contains some pyrite, apatite.
		Vitrinite	Ca(16), Fe(160), Mn(8)	
	Fig. 22 - 25	Semi-fusinite/ fusinite	Al(2), Si(4), P(18), S(2), Ca(54), Fe(0.5)	Semi-fusinite/fusinite contains large quantities pyrite, apatite and aluminum silicates. Vitrinite contains organic sulphur and small amounts of aluminum silicates.
		Vitrinite	Al(0.5), Si(1.0), S(5.0), Ca(0.5), Ti(0.5)	

* Numbers in parentheses are X-ray intensities indicating the relative amounts of elements present. Relative intensities should only be compared between the semi-fusinite/fusinite and vitrinite of each sample.

TABLE 2 - continued

Coal	Data Source	Maceral	Elements Determined by EDXA	Comments
WMVB	Fig. 26 - 29	Semi-fusinite/ fusinite	Al(8), Si(10), P(4), S(1), Ca(10)	Semi-fusinite/fusinite have a greater mineral content than vitrinite. As same elements are present, the minerals for each maceral are very similar.
		Vitrinite	Al(0.5), Si(12), P(1.5), S(2), Ca(2)	
	Fig. 30 - 33	Fusinite	Al(8), Si(11), S(2.5)	Fusinite probably contains organic sulphur. Mineral content of vitrinite less than that of fusinite.
		Vitrinite	Al(1), Si(1.5), S(2)	
EHVB	Fig. 41 - 44	Semi-fusinite/ fusinite	Al(5), Si(9), S(8), Fe(10)	Semi-fusinite/fusinite contains iron sulphides and aluminum silicates. Vitrinite contains less iron and calcium therefore sulphur must be organic in nature.
		Vitrinite	Si(0.5), S(6), Ca(1.5), Fe(0.5)	
	Fig. 45 - 48	Semi-fusinite/ fusinite	Al(4), Si(6), S(2), Fe(9)	Concentration of mineral phase in vitrinite less than in semi-fusinite. However, sulphur level is equivalent in the two macerals. This suggests vitrinite contains organic sulphur.
		Vitrinite	Al(0.5), Si(1.5), S(3), Ca(<0.5), Fe(1.0)	

APPENDIX A

Literature Review of Electron Microscopy Methods for Coal Characterization

February 1985

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1. INTRODUCTION

This section of the report presents a literature review of the current status of electron microscopy methods with regard to characterizing coal. In particular the inorganic (mineral) and organic (maceral) components of coal. For the purposes of clarity the review is divided into three sections:

(i) sample preparation techniques for electron microscopy studies of coal;

(ii) scanning electron microscopy (SEM) studies of coal;

(iii) transmission and scanning transmission electron microscopy (TEM) studies of coal.

The present status and utility of each of these techniques will be reviewed. In each instance an estimation will be made of the methods potential in:

(i) maceral characterization;

(ii) mineral characterization;

It is also important to note that the discussion will focus on electron microscopy analyses of whole coals; that is, studies in which the maceral-mineral or partial relationships are preserved. Studies of ashed or pulverized coals will not be reviewed.

2. SAMPLE PREPARATION TECHNIQUES FOR ELECTRON MICROSCOPY STUDIES OF COAL

2.1 Sample Preparation Methods for Scanning Electron Microscopy Studies

J.T. McCartney[1,2] reported a technique for preparing specimens of coal for electron microscopy studies. In this method, the coal specimens were polished using standard polishing techniques. The samples were then etched for a short time (10 seconds to a few minutes) in a chromic acid solution. After washing and drying, the coal samples were dipped in polyvinyl formal solution. Upon evaporation of the solvent, a solution of nitrocellulose in butyl acetate was spread over the surface. The double film of Formvar and nitrocellulose was then peeled from the surface. The double film was viewed using an optical microscope and 1/8-inch ducts of 200-mesh screen, used for support at electron microscope specimens were placed over areas showing good structure. These were fastened to the Formvar side of the film with tape. The tape with the film and screens attached was placed in amyl acetate to dissolve traces of nitrocellulose film and adhesive from the tape. The screens were then removed from the Formvar replica which was dried before observation in the electron microscope. This technique produced replicas suitable for electron microscopy studies of coal. In particular, electron micrographs of replicated microspores and cell structure were obtained.

Although acceptable micrographs of coal and maceral structure using a replication method have been obtained, replication methods have not been employed extensively in coal microscopy studies. An alternate and simpler method involves the direct observation of coal surfaces. Virtually all SEM studies of coal now utilize this particular technique. The technique involves the preparation of crushed coal pellets or coal briquet as described in ASTM method D2797-72.[3] Once prepared, the pellets are polished by first using grinding abrasives followed by polishing abrasives. The surface is then coated with a thin layer of carbon or gold. This method allows for easy visualization of embedded mineral matter in coal. However, observation of maceral details in carbon coated samples is not

routine. To observe maceral detail the specimen must be as flat as possible to reduce the extent of secondary electron imaging resulting from topographical features. For instance, Everhart[4] has demonstrated that topographical features which change the surface inclination to the electron beam by only a few degrees can produce significant changes in the number of emitted secondary electrons.

2.2 Sample Preparation Method For Transmission Electron Microscopy Studies

To permit transmission of electrons, with a 100 kV accelerating potential, the coal must be thinned to a thickness of 1.0 μm or less. McCartney, Walline and Ergun[5] developed a method of preparing ultra thin sections of coal. Briefly, their method consisted of crushing coal to a minus 8 - mesh size followed by dispersal in a commercially available hard setting resin. The resin block was then microtomed with a diamond knife. The thinned sections were floated on to electron microscope grids. The method is not routine and requires that the operator develop the judgement necessary to successfully microtome different coal types. For instance, it was determined that the following empirical factors were important:

(i) a proper level of water in the microtome trough was necessary to allow the sections to float free from the knife edge and thus minimize folding and wrinkling;

(ii) to obtain acceptable thin sections, the knife angle to the coal face must be modified to suit the hardness of a particular coal. The optimum angle was discovered by trial and error;

(iii) compression and folding, due to the motion of the knife edge was observed to occur in some specimens. To some extent this could be prevented by exposing the thinned sample to the vapour of an organic solvent.

This method did yield samples of thinned high volatile bituminous and anthracite coal.

Hsieh,[6] encountered some difficulty with a microtoming procedure for producing thin sections of coal. In particular, it was discovered that the motion of the blade could easily remove in-situ mineral matter from macerals. Many of the polymeric binders were also found not to be stable in the electron beam. In some instances the blade fractured embedded minerals. This resulted in poor quality diffraction patterns. It would seem that microtoming is not a suitable method for producing thin samples for TEM studies of mineral phases in coals.

Another method[6] involves grinding of coals into fine powders followed by dispersal onto a copper grid. The ground coal is normally dispersed using alcohol. This method has been reported to have limited success, primarily because it is very difficult to grind powders with particle diameters of less than 1.0 μm.

Ion milling is one technique that has been demonstrated to produce thin sections of coal suitable for TEM studies. Harris and Yust[7,8] using this method have been successful with regard to viewing coal pores and minerals in an eastern Kentucky splint coal and an Illinois No. 6 coal. Hsieh[6] has also found the method useful for observing in-situ minerals in maceral groups. To use this method, small sections of coal are mounted on a glass slide and polished

to a thickness of less than 1 mm. The coal is then removed from the slide and ion milled. Ion milling was performed using argon gas and a liquid nitrogen cold stage to prevent thermal degradation. Argon ions were accelerated to 4-5 kV with an intensity of 50 - 100 microamps. Approximately two days were required to prepare a sample suitable for TEM work. Hsieh[6] indicated that the method requires further development work if it is to be used to prepare samples for maceral characterization. This researcher noted that the beam may cause ripples in the surface of the sample that could be mistaken for maceral structure.

3. SCANNING ELECTRON MICROSCOPY (SEM) STUDIES OF COAL

The SEM has been applied extensively to coal characterization and coal conversion processes. In particular, the SEM, coupled with an energy dispersive X-ray analyzer, (SEM/EDXA) has proven useful for the characterization of the mineral content of coal. In addition, attempts have been made to use the SEM to obtain detailed images of coal macerals. The purpose of these types of studies was to supplement the data obtained using standard reflected light microscopy. Use of SEM/EDXA techniques to study coal mineral matter will now be considered.

3.1 Characterization of Coal Mineral Content by SEM/EDXA

Gluskotter[9] has suggested that the term "mineral matter" as applied to coals is somewhat misleading. The term usually refers to the inorganic (non-coal) material found in coal as mineral phases. However, strictly applied, this definition excludes elements such as carbon, nitrogen, oxygen, hydrogen and sulphur. It is therefore important to note that these elements are also common to both the inorganic (mineral) and organic (maceral) components of coal. For instance, in the

mineral phase, hydrogen maybe detected as water or hydroxy silicates; sulphur as sulphate; nitrogen as nitrate and carbon as carbonate. Any mineral analysis must then distinguish between the inorganic and organic nature of these elements.

SEM/EDXA methods have been used to determine the identity of the mineral constituents of coal. The method has not been sufficiently developed to the extent that it may be used to estimate qualitatively and quantitatively the mineral composition and distribution in a particular coal source.

Table 1 lists many of the minerals found in most coals. The SEM/EDXA method does not allow for direct identification of these minerals. Rather, it allows detection and estimation of the various elements within a mineral phase. Mineral identification requires a correlation of observed elements with likely mineral types.

Boating and Phillips[10] have used the SEM and the electron microprobe to study coal surfaces. This study focussed primarily upon the distribution of sulphur in several coal types. Sulphur distributions from electron microprobe analysis were obtained. This led to the conclusion that organic sulphur is evenly distributed within coal macerals. The SEM/EDXA system facilitated the identification of pyrite and thus allowed for the characterization of pyritic sulphur.

Augustyn, Iley and Marsh[11] used the SEM/EDXA system to study the mineral content of brown coals. For all brown coals studies, aluminum, silicon, sulphur, calcium, potassium, titanium and zinc were detected. It was suggested that these elements probably exist in brown coals as silica, silicates, alumino-silicates, carbonates, sulphates, sulphides and chlorides.

TABLE 1

MINERALS COMMONLY FOUND IN COALS

Silica minerals	Quartz (trigonal), SiO_2
Chlorite	$(Mg,Al,Fe)_{12}\{(Si,Al)_8O_{20}\}(OH)_{16}$
Serpentine	$Mg_3(Si_2O_5)(OH)_4$
Clay Minerals	Kaolinite group, $Al_4(Si_4O_{10})(OH)_8$
	Illite, $K_{1-1.5}Al_4(Si_{7-6.5}Al_{1-15}O_{20})(OH)_4$
	Montmorillonite group, $(\frac{1}{2}Ca,Na)_{0.7}(Al,Mg,Fe)_4$ $(Si,Al)_8O_{20}(OH)_4 \cdot nH_2O$
Feldspar Group	Alkali Feldspars, $(K,Na)(AlSi_3O_8)$
	Plagioclase, $Na(AlSi_3O_8)$ or $Ca(Al_2Si_2O_8)$
Sulphates	Gypsum, $CaSO_4 \cdot 2H_2O$
	Annydrite, $CaSO_4$
	Hemihydrate, $CaSO_4 \cdot \frac{1}{2}H_2O$
	Barytes, $BaSO_4$
Sulphides	Pyrite, FeS_2
	Marcasite, (orthorhombic), FeS_2
	Pyrrhotite, $Fe_{1-x}S$
	Chalcopyrite, $CuFeS_2$
	Sphalerite, ZnS

TABLE 1 (Cont'd)

Carbonates	Ankerite, $Ca(Fe,Mg)(CO_3)_2$
	Calcite, $CaCO_3$ (trigonal)
	Aragonite, $CaCO_3$ (orthorhombic)
	Magnesite, $MgCO_3$
	Rhodochrosite, $MnCO_3$
	Siderite, $FeCO_3$
	Dolomite, $CaMg(CO_3)_2$
	Strontianite, $SrCO_3$
	Witherite, $BaCO_3$
Rutile	TiO_2
Chloride	Halite, NaCl
	Sylvite, KCl
Accessory Minerals Occurring in Minor Quantities	Feldspar, $(K,Na)_2O.Al_2O_3 \cdot 6SiO_2$
	Garnet, $3CaCO_3 \cdot Al_2O_3 \cdot 3SiO_2$
	Hornblende, $CaO \cdot 3FeO \cdot 4SiO_2$
	Gypsum, $CaSO_4 \cdot 2H_2O$
	Apatite, $9CaO \cdot 3P_2O_5 \cdot CaF_2$
	Zircon, $ZrSiO_4$
	Diaspore, $Al_2O_3 \cdot H_2O$
	Magnetite, Fe_3O_4
	Hematite, Fe_2O_3

Saunders[12] determined the distribution and nature of sodium and chlorine in coal utilizing SEM and electron microprobe techniques. Quantitative microanalysis of sodium and chlorine, in three maceral groups, (vitrinite, exinite and inertinite) was performed using an electron microprobe. The general morphology of the coals was examined in the SEM. Analysis of maceral groups showed that the chlorine was present mainly in vitrinite bands, and in the vitrinite which surrounds microspores and megaspores in exinite-rich areas. The sodium distribution followed the same general trends as that observed for chlorine. In general, the SEM was used in this study to observe in-situ sodium chloride crystallites within a particular maceral group.

Finkelman and Stanton[13,14] utilized a SEM/EDXA system to develop a procedure for the in-situ analysis of mineral grains in polished sections of coal. The thrust of the work was to relate minerals, trace elements and macerals in a coal specimen. A SEM was used to study the in-situ accessory minerals of polished blocks and pellets of a high volatile bituminous coal.

The high resolution of the SEM permitted the detection of submicron mineral grains which were subsequently analyzed by a EDXA system. Minerals such as rutile, zircon and rare-earth bearing minerals were detected. Particles of 1-5 μm diameter, such as iron-rich chromite and nickel silicate were observed as rims on quartz grains. The SEM also had utility with regard to the observation of grain morphology and mineral intergrowth.

More recently,[15,16] SEM automatic image analysis of coal mineralogies has been developed. This was accomplished by interfacing the Le Mont beam control system with an SEM

equipped with a software-based multichannel analyzer-energy dispersive spectrometer X-ray analyzer. A technique was developed for determining the size, shape, composition and relative amounts of in-situ minerals in washed coals. The technical details of the system will not be discussed in this review. The reader is referred to references 15 and 16 for this information. For this technique, one gram of crushed coal is prepared in pellet form following ASTM standard methods D311, D346 and D2234. However, the surface of the pellets were rough ground with metal grids impregnated with boron nitride and lightly polished with diamond paste. The use of boron nitride and diamond pastes, rather than standard polishing materials (i.e. alumina) prevented the imaging of polishing materials in the back scattered electron mode. For the mineralogical analysis of coals, an inverted back-scattered electron image was used as this image provided the best contrast between minerals and macerals. The beam control system utilized this contrast to identify a mineral particle and subsequently to determine the particle area. Once the electron beam was on a particle, an energy dispersive X-ray spectrum was accumulated. The total counts of 11 elements (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti and Fe) were then normalized to 100%.

A computer was employed to classify the particle into one of 29 categories of minerals. The calculation of the weight percentage of a given category in the total mineral matter was based on the sum of the areas of particles of that category multiplied by the density.

In addition to information on the weight proportions of the various minerals, data were provided on particle size ranges for different mineral categories.

The following advantages were listed for the scanning

electron microscope automatic image analysis technique:

(i) it can be applied directly to in-situ coal minerals;

(ii) major and minor mineral phases can be determined;

(iii) particle size information is obtainable;

(iv) the analysis is not time-prohibitive;

(v) the analysis does not require calibration curves or reference spectra.

The authors of this research were optimistic that the technique could be developed as a quantitative method for the mineral analysis of coal. However, further work is required to solve the following problems:

(1) a method for accurately determining the volume fractions of minerals is required;

(2) problems were encountered whenever several mineral types resided within a small volume element;

(3) problems were encountered with distinguishing sulphides from sulphates and iron oxides from iron carbonates.

Timmer and van der Burgh[17] have recently reported on an automated system for determining organic sulphur in coal using SEM/EDXA methods. This was accomplished by producing crushed coal pellets (0.5 mm diameter) that could be fixed to a computer-controlled automated SEM sample stage. The computer was interfaced with an EDXA system. This arrangement allowed samples to be moved across the fixed electron

beam along a programmed path, on which analyses were carried out at predetermined intervals in very small areas. Organic sulphur was distinguished from inorganic sulphur by instructing the computer to ignore sulphur at all points where calcium or iron exceeded threshold values. A total of 1000 measurements per crushed coal pellet were taken. This analytical method allowed for the rapid and accurate determination of organic sulphur in coal.

3.2 Characterization of Coke and Coal Macerals by SEM/EDXA

Scanning electron microscopy methods for the characterization of the organic components of coal are less developed than mineral analysis methods. The SEM has proven useful for observing topographical features of coals and cokes. However, achieving the required contrast necessary to observe maceral features in flat surfaces is not routine.

Augustyn, Iley and March[11] used the scanning electron microscope to study brown coals. Small specimens were carbon coated and examined using a Stereoscan microscope (Cambridge Instrument Co.). These samples were not polished flat and therefore the micrographs in this paper illustrate topographical features. Many of the coals examined, in this manner, exhibited cellular structure. These researchers concluded that the SEM could therefore be used to supplement petrographic methods.

Saunders[12] also reported using the scanning electron microscope to examine coal macerals. In this particular study the coal samples were polished flat. The three main maceral groups: vitrinite, exinite and inertinite, were first identified by optical microscopy, with subsequent characterization using the SEM. The vitrinite maceral group appeared mainly

as homogeneous bands within the coals examined, and individual macerals could not be distinguished. The exinite group was shown to consist of sporinite in the form of large megaspores. These spores were easily distinguished and analyzed using a small scan raster on several areas along the spore.

The inertinite group was found to be mainly present as the maceral semi-fusinite. The SEM micrographs showed residual cell structure of wood filled with mineral matter.

Nandi, Montgomery and Martin[18] have also evaluated the utility of the SEM for identification of coal macerals. This was accomplished by comparing optical and SEM micrographs of identical maceral groups. In this study, whole samples of coal were polished flat and the following conclusions were reached:

(i) for the coal types examined, the macerals vitrinite, exinite, fusinite and semi-fusinite were visible in the secondary electron image;

(ii) the backscattered image was useful for detecting mineral phases.

The previous text has outlined the extent to which the SEM has been used to view coal macerals. It should be apparent to the reader that a very limited amount of work has been done in this area. Part of the problem is due to the fact that these studies are purely academic. Little effort has been expended with regard to expanding the potential petrographic role of the SEM. Part of the problem also resides with the microscope manufacturers. Using new computer imaging technology now available, microscopes could be designed with an enhanced capability for viewing coal macerals. However, there is a very limited market for this

application and therefore it is understandable why this option is not available.

The SEM has also been used extensively in the study of coke. Frigg and Wolff[19] examined two samples of coke using the SEM, to show the potential of the instrument for coal research. Coke made from coking coal is known to behave differently, during combustion, coke made from high volatile coal. These differences were observable using the SEM. For instance, partially coked samples of these two coals exhibited differences in the behaviour of the lamellae that were not detectable by light microscopy.

The SEM has been applied to metallurgical cokes and residues from rapid pyrolysis of coals.[20] The SEM was used to observe the following:

(i) the pore structure in cokes formed at 700^{o}C;

(ii) formation of bubble structures at 1000^{o}C. (This was attributed to rapid gas evolution;)

(iii) a fusain inclusion in the 1000^{o}C coke. (This was attributed to rapid gasification);

(iv) a difference in pore formation in residues produced from medium volatile and high volatile coals.

Adair et al[21] employed the SEM to study the gasification of a blast-furnace coke. During the controlled gasification of a metallurgical coke, changes in the surface topography were monitored using SEM. The gasification was observed to proceed via a process of surface pitting and fissure formation. Increasing temperature encouraged fissuring, with surface pitting occurring at the positions of cataly-

tically-active impurities. Thus, the SEM proved to be extremely useful for studying the gasification of cokes.

Hays, Patrick and Walker[22] have used the SEM to study the surface of fractured and etched metallurgical coke. Epoxy resin-impregnated polished surfaces of uncrushed specimens were etched in a low temperature plasma. The surfaces were then gold-coated and examined in the SEM. Atomic oxygen etching of metallurgical cokes resulted in pitted and channelled surfaces. By viewing the same area before and after etching, it was established that the surface texture of etched coke was dependent on the type of anisotropic component present.

Briefly, in the formation of graphite the plastic range is viewed as a temperature zone in which the lamellar molecules of the isotropic fluid phase assemble to form liquid crystals. Polymerization increases within the liquid crystals as carbonization proceeds. This results in a stabilized structure and the growth of spherical anisotropic units. The number of these units increases until the fluid phase is converted to semi-coke. Atomic oxygen etching of metallurgical cokes was employed with the expectation that the less etch-resistant portions of the structure would be removed, exposing the more crystalline structure. The SEM was useful for indicating the extent to which this process varied with coal rank. The SEM, with its large depth of focus, was utilized to view the three dimensional nature of the structural units (i.e. building blocks) from which metallurgical cokes are assembled. It was determined that the coke components could be classified into four categories; flat, lamellar, intermediate and granular, according to their appearance in the fracture surface.

This research was continued by these workers with the aim of

showing how the examination of fractured and etched surfaces in an SEM may be used to characterize a variety of cokes and carbons.[23,24] SEM studies of fractured and etched coke surfaces led to the development of a method for quantifying the carbon textural composition of cokes by point-counting of etched surfaces (using the SEM). Attempts were made to develop relationships between the textural compositions of cokes and their strength and pore structure parameters. The following conclusions were reached:

1. features visible on tensile fractured coke surfaces can readily be identified with coke-carbon textural components, revealed by scanning electron microscopy of atomic-oxygen-etched surfaces of polished coke sections;

2. the marked variations in the appearance of fracture features suggested that the coke texture composition may contribute to the variation in tensile strength;

3. the carbon texture composition of cokes can be quantified by point-counting of etched surfaces using an SEM;

4. preliminary studies showed that relationships between the textural composition and the strength and structural parameters of cokes can be demonstrated;

5. no generally applicable relationship exists between coke-pore structural parameters and the-dilatation or reflectance of the blend carbonized. Linear relationships, however, can be observed in special limited cases, particularly for two-component coal blends.

4. TRANSMISSION ELECTRON MICROSCOPY (TEM STUDIES OF COAL)

4.1 Transmission Electron Microscopy Studies of Coal Minerals

Application of the TEM to the study of coal is comparatively more developed than that of the SEM. Indeed, one of the earliest studies was reported more than 35 years ago.[1 25] The TEM requires that the sample take the form of a thin foil, typically 10 - 50 nm thick. Coal is an ideal candidate for TEM studies. Thin sections can be prepared and since the electron densities of the organic and mineral components are significantly different, these phases are easily distinguishable. In addition, the resolution of the TEM is such that particles into the 10 nm range may be observed, and crystal structure determination is made possible by means of electron diffraction. This section of the literature review will discuss coal mineral identification using the TEM.

The submicron mineral component of vitrinite was studied by TEM.[26] Fragments of vitrinite were microscopically separated, thinned by ion bombardment and examined in the TEM. Micrographs of the macerals showed a profusion of mineral particles in the size range below 1 μm. The particles appeared to be of two principal sizes, particles less than 30 nm and a population of smaller particles. These smaller particles accounted for approximately one-third of the total vitrinite surface area. X-ray diffraction data suggested that the principal mineral components were clays and calcium carbonate.

Harris and Yust[7] utilized a scanning transmission electron microscope (STEM) in conjunction with an EDXA system to study the mineral phases in milled coals. Elements such as Al, Si, Fe, S, Ca and K were detected. These elements were attributed to the presence of clays, pyrite, gypsum,

calcite and quartz. However further analyses of the mineral content of spore cavities indicated the presence of titanium dioxide. In addition to these mineral types, numerous submicron minerals were detected among the various macerals.

Allen and Vander Sande[26] have also used the STEM for submicron mineral analyses of coal. For the purposes of this study the coal was finely ground and dispersed on a copper grid. These researchers demonstrated that the STEM is well suited for the characterization of submicron size mineral matter in coal, and inorganic elements atomically bound in the organic matrix. For the three coal types studied, a random survey was made of mineral inclusions with diameters up to 100 nm. The results indicated that for the three coals examined, the submicron minerals are different from the larger mineral types.

Rowlands and Smart[27] have reported using the TEM to determine the mineralogical content of coal. These researchers ground the coal to 20 μm. Specimens for analysis were prepared by placing small amounts of the ground coal into centrifuge tubes and forming a suspension in distilled water. Small amounts of the suspensions were removed and dropped onto microslides. The droplets were evaporated to dryness, to yield a thin film of particles deposited on the slides. The films were coated with polyvinyl acetate, applied within an open centred square of adhesive tape. When the polyvinyl acetate was nearly dry, the squares were detached from the slides, removing the particle impregnated films with them. The squares were then overturned, covered with a thin carbon film, and then placed in a hot water bath to dissolve the polyvinyl acetate. This resulted in a film of carbon impregnated with mineral particles. These films were then mounted on 200 mesh gold and copper electron microscope grids. This prep-

aration was performed to ensure good conductivity of the sample, and thus reduce melting, evaporation and migration effects. TEM/EDXA analysis indicated that the majority of the particles were below 5 μm in diameter. TEM/EDXA and related area diffraction identified minerals such as illite, kaolinite, quartz, ion oxide and rutile. These data were used in conjunction with bulk chemical analyses to determine the mineral phases present in the coals.

Perhaps the most recent and extensive study of minerals in coal by TEM has been performed by Wert and Hsieh[6,29]. These researchers principally used ion milling to produce thin samples of coal for transmission electron microscopy studies. The ion milling technique involved slicing off a small section of coal (a few millimetres in size), which was then thinned using an Argon plasma. To avoid long milling times, samples were first hand-ground to a thickness of 50 μm. The most important difficulty with ion milling was that changes were induced by heating caused by the ion beam. For instance, this study demonstrated that localized heating effects from ion milling transformed pyrite to pyrrhotite. To overcome this, the specimens were cooled to -20 C. Principal attention was directed to the characterization of sulphides and clays. General topography, crystal type, planar spacing and chemical composition were determined using bright and dark field imaging, electron diffraction and energy dispersive x-ray spectrometry.

A companion study conducted by Wert and Hsieh[28,29] centred on determining the inorganic sulphur present in Illinois coal. This study discovered that pyrite was present in three forms within the coal. It was found as massive polycrystalline aggregates, as pyrite agglomerates in the form of framboids, and also as isolated single crystals. Other inorganic sul-

phides such as ZnS, CdS, PbS and FeAsS were identified. These researchers concluded that identification of the sulphides using the TEM is not difficult. Diffraction techniques can be used to determine crystal structure data. However, it is important to note that minerals must be thinned so that they are sufficiently transparent to the electron beam.

Allen and Vander Sande[30] have recently reported on the use of a STEM to obtain quantitative information about the ultrafine (200 nm diameter) mineral inclusions in several coals, and to examine the inorganic elements atomically bound into the organic matrices of these coals. Samples of three different coals were examined in this study; a lignite, a semianthracite, and a sample of pulverized bituminous coal. For these studies, the coal was ground to a fine powder using a mortar and pestle. The particles were then dispersed on a carbon-coated copper grid. Specimens prepared in this manner were considered to be well suited for STEM viewing as compared to ion milled samples. The advantages were in the absence of artifacts (as introduced by ion milling) and in the ease of preparation. In addition, nearly all the particles on the grid have some area transparent to the electron beam, and a larger volume of thinned coal sample was potentially available for STEM analysis. The STEM analysis, automated image analysis, AIA, was accomplished using a software routine developed by U.S. Steel. The AIA program was interfaced with an electron microprobe, fitted with an energy dispersive X-ray system, a backscattered electron detector and a digital beam control. The system analyzed the distribution of mineral species in the size range from 300 μm to 0.2 μm. Thus, by using both STEM and AIA techniques, analysis of coal mineral matter was possible over a particle size range from 300 μm to 2 nm. For all three coals, the predominant mineral species observed in the 0.2 μm size range would

not have been predicted from the results of standard chemical analyses.

4.2 Transmission and Scanning Transmission Electron Microscopy Studies of Coal Macerals

Application of the SEM and TEM to coal maceral characterization is not as developed as in coal mineral characterization. The primary reason for this is due to difficulties in the preparation of samples which are sufficiently transparent to the electron beam. Degrees of success have been achieved with application of the ion milling method. However, at best it is a "hit or miss" matter as to whether maceral structural detail is observable using these techniques.

Perhaps one of the first replication studies to produce samples for TEM analyses of coals was performed by J.T. McCartney[1] in 1949. This researcher produced replicas from coal surfaces that had been etched by chromic acid. The purpose of the chemical etching was to produce sufficient relief in order that the maceral detail could be transferred to the replica. The success of this method is obviously dependent upon whether each of the maceral types present in a coal chemically etches at different rates (i.e. to produce the necessary relief). Micrographs of replicas were obtained that clearly exhibited microspore and plant cell material in vitrinite. In a later study, McCartney[31] examined ultra-thin sections of vitrinite in coal, using transmission electron microscopy. These researchers cut thin sections of coal using a diamond blade. Interpretation of micrographs of thin sections of coal was performed with the realization that microtoming is known to introduce artifacts. Using the methods described, cell structure was observed in samples of semi-anthracite, high volatile bituminous and anthracite coal. All sizes were estimated, and

some concern was expressed over the distortion of the cells due to microtoming.

Pregermain and Guillemot[32] also used a microtome to cut thin sections of coal (500 - 2000 nm). Structures were observed in vitrinites consisting of grains ranging in average size from 25 nm in a lignite, to 10 nm in a semianthracite. Brown and Taylor[33] further examined the question of artifacts introduced into thin sections of coal produced by cutting features. These researchers were able to observe such effects as exinite-vitrinite boundaries and mineral grains.

A more extensive study was conducted of microtomed sections of coal by McCartney et al[2]. These workers indicated that careful microtoming of coals could minimize artifacts. The following was observed in their transmission electron microscopy study:

(i) components such as vitrinite, exinite and granular micrinite were identified;

(ii) a megapore was observed in one ultra-thin section;

(iii) crystalline platelets of graphite formed from aromatic layer clusters were detected. This was assumed to form during metamorphosis of a meta-anthracite.

More recently, Harris and Yust[7,8] have conducted a study of the ultrafine structure of coal. These workers used the TEM to observe microstructure and porosity of ion milled samples. The observed porosity varied with the maceral type such that the finest pores (2 - 5 nm) were located in vitrinite, with the larger pores (40- 500 nm) associated with the macerals exinite and vitrinite.

Characterization of huminite macerals has been studied by Taylor et al.[34] Thin sections of a brown coal were cut using a microtome and then viewed in the TEM. This study indicated that huminite macerals are not the most distinctive entity within brown coal. It was observed that differences of material and in texture exist in the huminite group. For instance, considerable void spaces were detected in some macerals. This observation is consistent with the compressibility and deformability of brown coal during briquetting.

The use of a electron staining technique revealed an enhanced layer structure, presumed to be formed from cell walls. Part of this enhancement was attributed to the higher uptake of heavy metal solutions by gelified, as compared to ungelified huminite.

Other physical features of coal, such as porosity have been examined using the TEM.[7] Channel-like pores were observed in ion milled samples of a high volatile bituminous coal. The porosity observed was classified into two types. The first type consisted of relatively large pores found associated with the spore exines. These pores were observed to be emanating from the interface of the spore exines with inertinite. The majority of these pores were found to contain small spherical particles thought to be the catalysts for their development. The sizes of the group of pores ranged from 20 to 100 nm in diameter, spanning the (2 - 50 nm) and macropore (750 nm) classification. The second type of porosity detected exists within the inertinite and appeared to form an intimate mixture with the exinite. All of these pores were classified as mesospores. This porosity was continuous and thus was considered to contribute to the permeability of the coal. Finally, the study showed that the observed porosity in the exinite and

inertinite fractions of the coal fall within the mesospore range. Thus, it was concluded that if any microporosity (<2 nm) exists in this coal it must lie within the exinite and inertinite fractions.

Macerals in coal have also been examined using transmission electron microscopy by Hsieh.[6] The purpose of this research was aimed at evaluating ion milling as a technique for sample preparation. This researcher indicated that ion milling can produce minute ripples over the entire coal surface. The rippling may be caused by a combination of the maceral structure and selective sputtering. In particular, in the samples observed, rippling as well as internal voids and boundaries were detected in concentrated masses. These micro-voids were about 10 nm in size and it was not possible to distinguish what was intrinsic to the coal and what was produced by ion bombardment. Thus, careful evaluation of samples produced by ion milling is required.

High resolution transmission electron microscopy has been applied recently with the purpose of understanding carbonization and graphitization of carbonaceous materials.[35,36,37] Organic matter evolves towards pure carbon either by coalification or carbonization. During these processes, as the oxygen and hydrogen content decrease, aromatic planar structures form. Due to the hexagonal structure of the aromatic molecule, these aromatic structures become periodic and thus scatter electrons in orderly fashion. Consequently, the lattice imaging and dark field imaging capacity of the TEM may be used to study carbonization. Lattice imaging involves defocussing of the objective lens to yield a scattered beam that interferes with the unscattered transmitted beam. Fringes may be obtained in the image plane. The period of the fringes is equal to that of the (hkl) family of lattice planes which are enlarged by the magnifying power of the lens.

If suitable instrumental conditions are chosen, the number of planes in a layered aromatic structure and the diameter of the basic structural unit can be determined. In dark-field imaging, a single scattered beam is used for imaging. The emitting area of the object appears bright on a dark field. The exact details required to utilize dark-field imaging for carbonaceous materials are fully discussed in reference 38.

These techniques have been used to study coalification and carbonization processes.

During coalification and carbonization, the randomly distributed poly-aromatic units are small (1 nm). Probably 4 to 12 rings are connected by non-aromatic functional groups. As H_2O, CO_2, light hydrocarbons, and tars are released, the poly-aromatic units concentrate. TEM studies indicate that the poly-aromatic units do not grow in size. As most of the tar is released, a textural change occurs that corresponds to the formation of preferred local orientations. Dark field imaging was used to obtain information concerning molecular orientation of aromatic units with respect to a crystallographic axis. These types of data were then interpreted in terms of coalification and carbonization processes.

5. SUMMARY

The preceding text has reviewed the application of electron optical studies of coals and cokes. An attempt has been made to present the important milestones of electron optical/coal research. Upon reviewing the literature, it became evident that the scope of studies involving the application of the TEM and SEM to coal research is somewhat non-directional. Considerable effort has been applied to the studies of cokes, carbonization and coal minerals, but very little with respect to coal macerals and porosity. Although, papers on these subjects

were presented in the review, they were found to be the exception rather than the rule. Most of these papers present short-term studies of the application of scanning electron microscopy and transmission electron microscopy to coal maceral and coal pore characterization. Presumably, this is due to the difficulty and labour-intensiveness of such studies.

As coal macerals are most routinely identified by optical microscopy, it would seem appropriate and necessary for more electron optical research to focus on coal pore characterization. This type of study has the potential of determining the following:

(i) pore size dependence on coal rank and maceral type;

(ii) orientation of pores in coals and whether they are interconnected or randomly-distributed. The presence of interconnected pores implies good porosity of the coal. This is important with regard to liquefication and combustion;

(iii) the importance of pores for determining the efficiency of coal conversion processes. Interconnected pores allow for conduction of gas and liquid phases both out of and into the coal. This has a significant potential for predicting the efficiency of coal processes dependent upon this characteristic.

It would therefore seem reasonable to conclude that more research is required to document coal porosity and its relevance to coal conversion processes. This could be accomplished by further electron microscope studies.

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APPENDIX B

Figures 1 to 84
Micrographs (SEM, TEM and Optical) and
Energy Dispersive X-Ray Analyses

LEGEND FOR MICROGRAPHS

F - FUSINITE

SF - SEMI-FUSINITE

SF/F - SEMI-FUSINITE/FUSINITE

V - VITRINITE

E - EXINITE

EB - EPOXY BINDER

Figure 1. Optical micrograph (reflected light, dry objective) of a western low volatile bituminous coal.

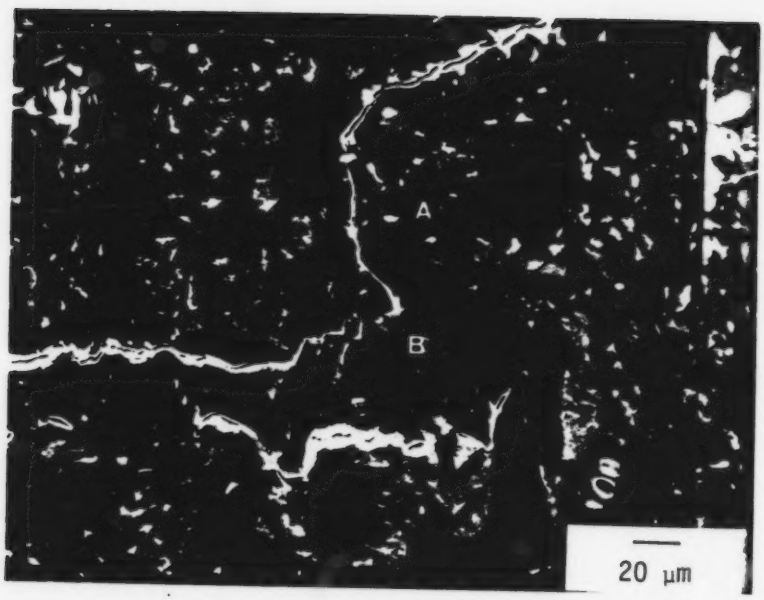

Figure 2. Scanning electron micrograph of a western low volatile bituminous coal. A and B indicate the areas where the EDXA spectra in figures 3 and 4 were acquired.

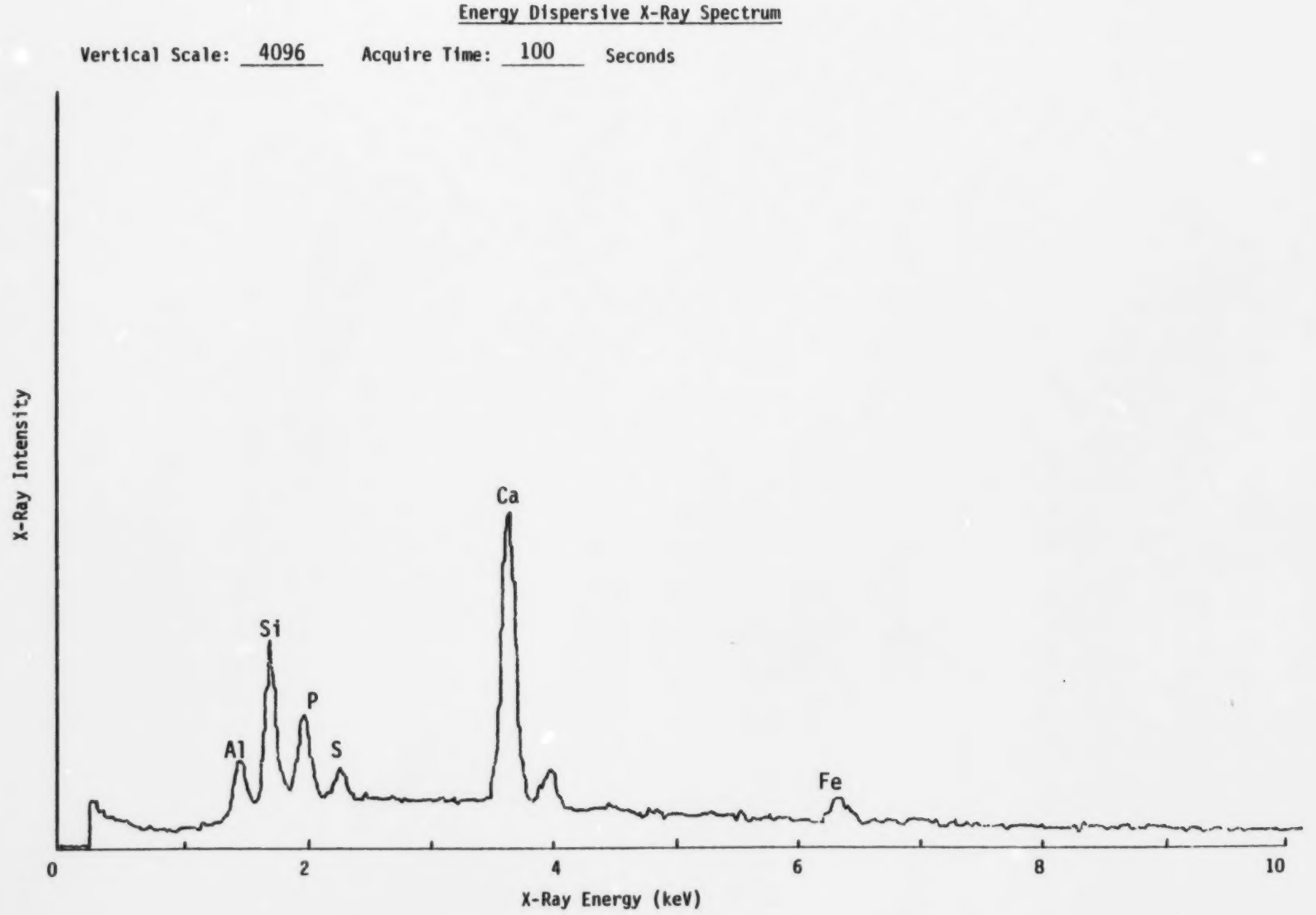

Figure 3. EDXA spectrum acquired from area A as indicated in figure 2.

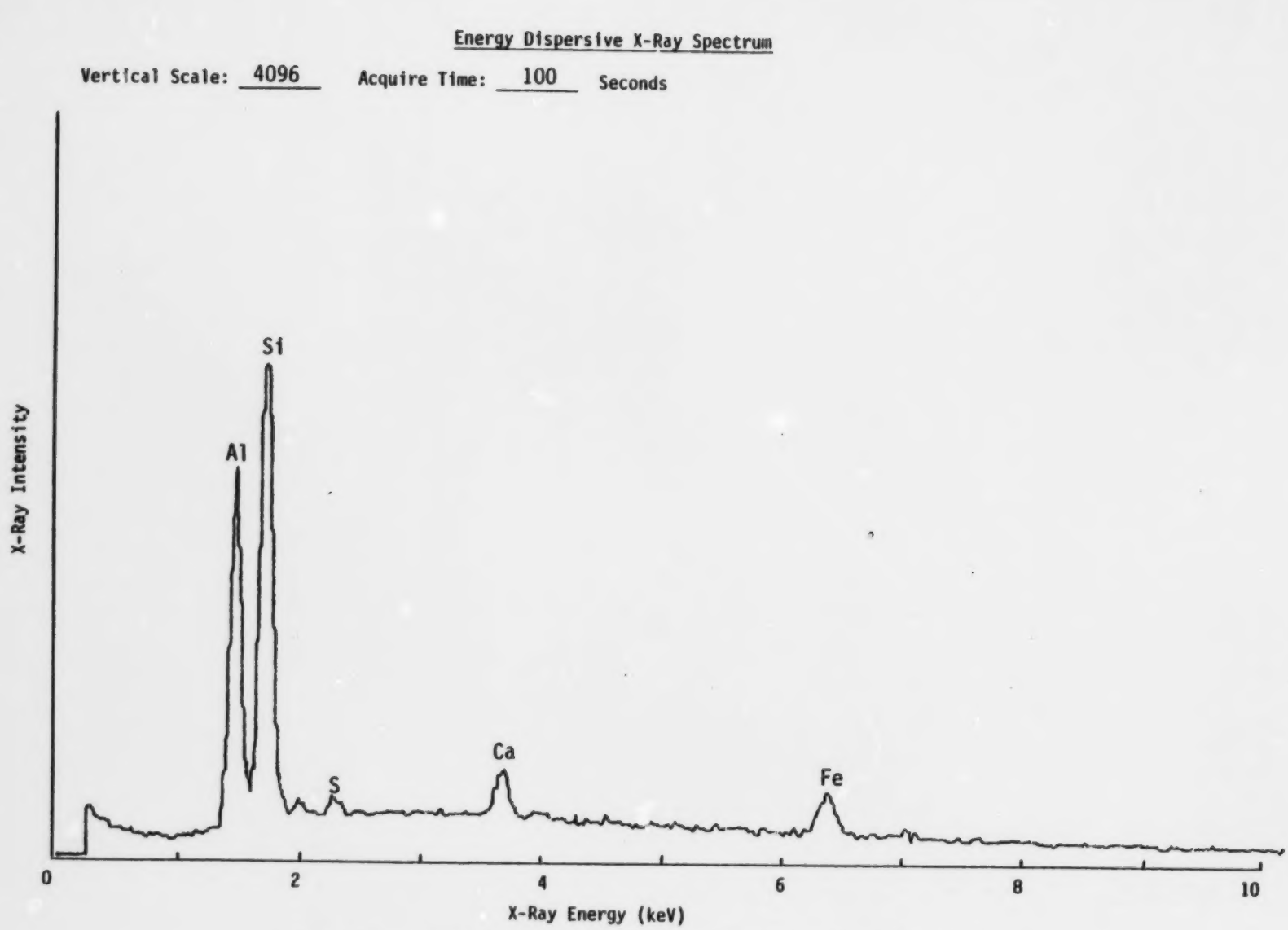

Figure 4. EDXA spectrum of area B as indicated in figure 2.

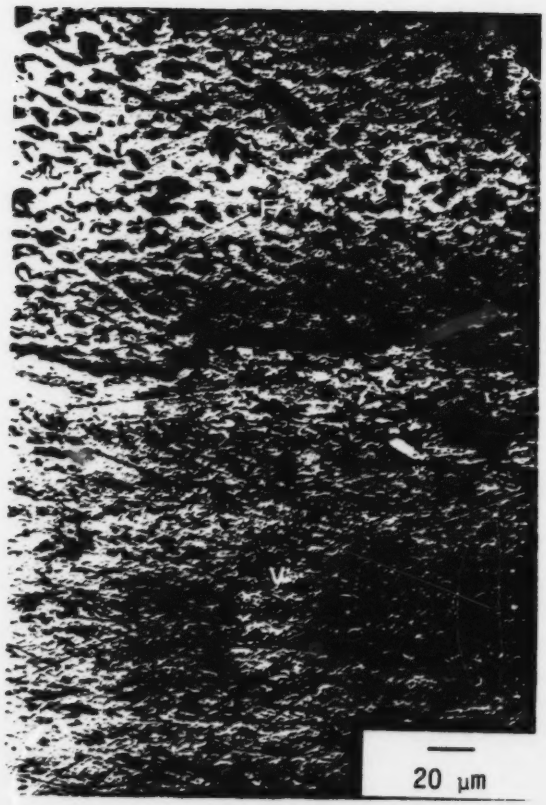

Figure 5. Optical micrograph (reflected light, dry objective) of a western low volatile bituminous coal.

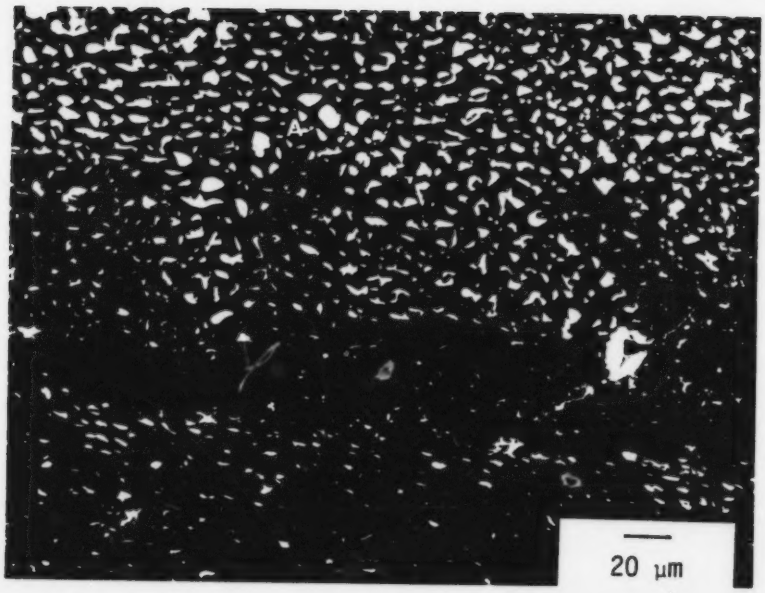

Figure 6. Scanning electron micrograph of a western low volatile bituminous coal. A indicates the area where the EDXA spectra in figure 7 was acquired.

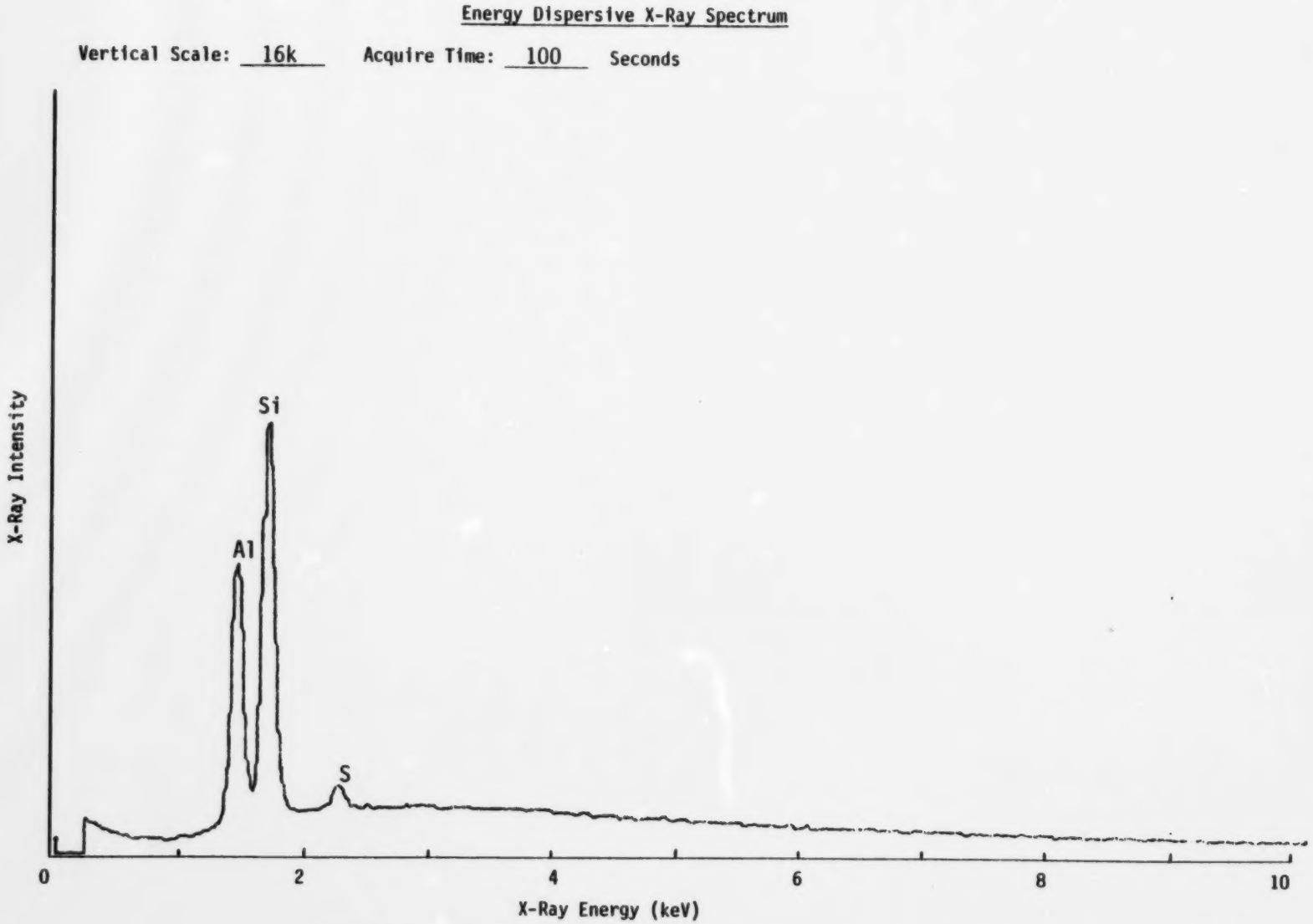

Figure 7. EDXA spectrum of area A as indicated in figure 6.

Figure 8. Optical micrograph (reflected light, dry objective) of a western low volatile bituminous coal.

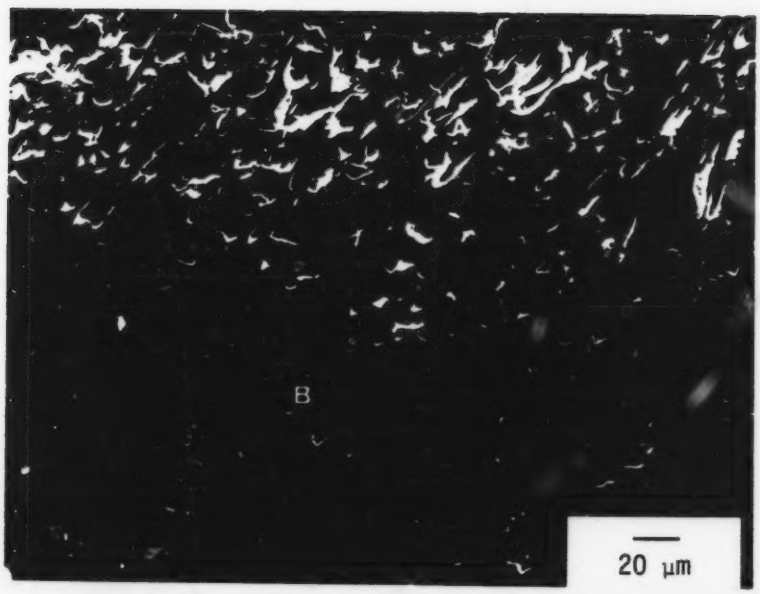

Figure 9. Scanning electron micrograph of a western low volatile bituminous coal. A and B indicate the areas where the EDXA spectra in figures 10 and 11 were acquired.

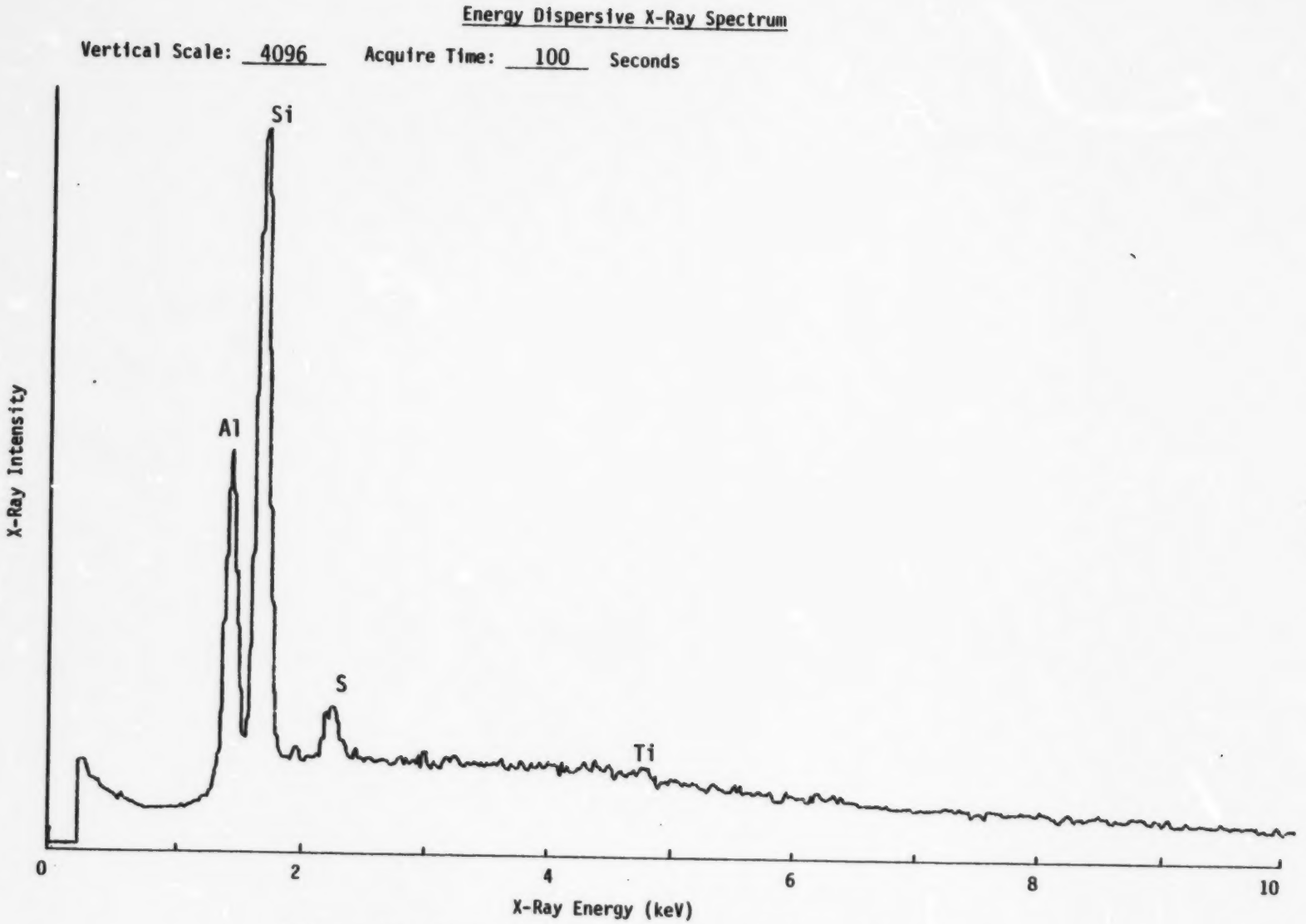

Figure 10. EDXA spectrum of area A as indicated in figure 9.

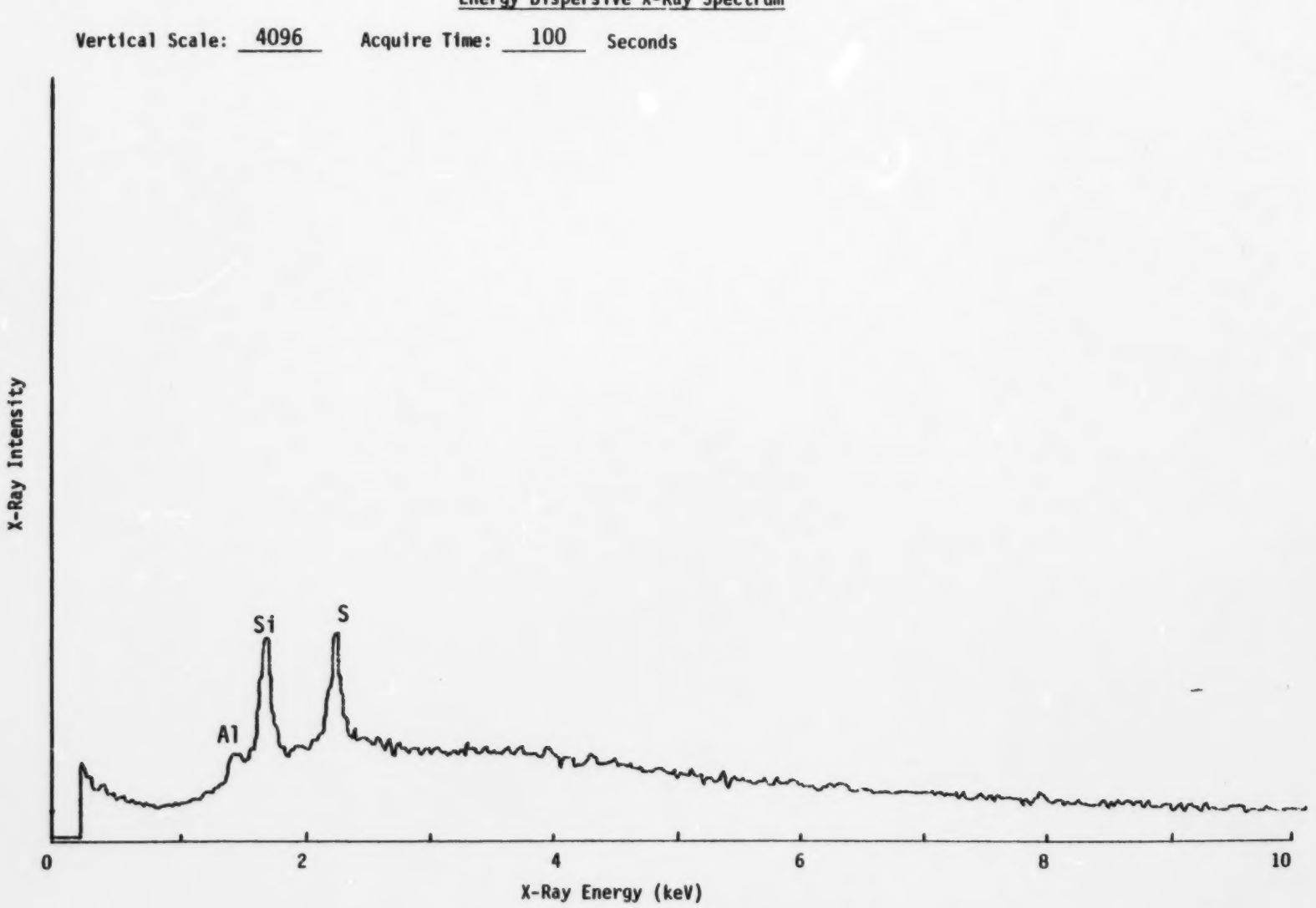

Figure 11. EDXA spectrum of area B as indicated in figure 9.

Figure 12. Optical micrograph (reflected light, dry objective) of a western low volatile bituminous coal.

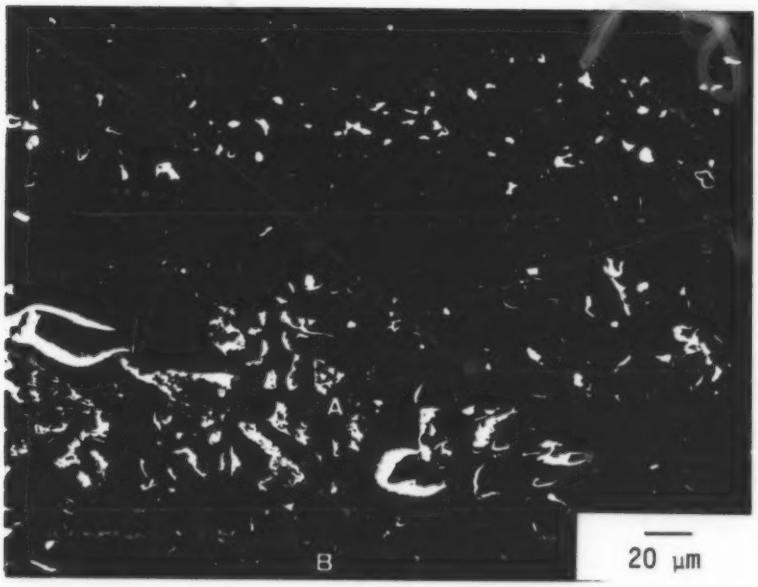

Figure 13. Scanning electron micrograph of a western low volatile bituminous coal. A and B indicate the areas where the EDXA spectra in figures 14 and 14a were acquired.

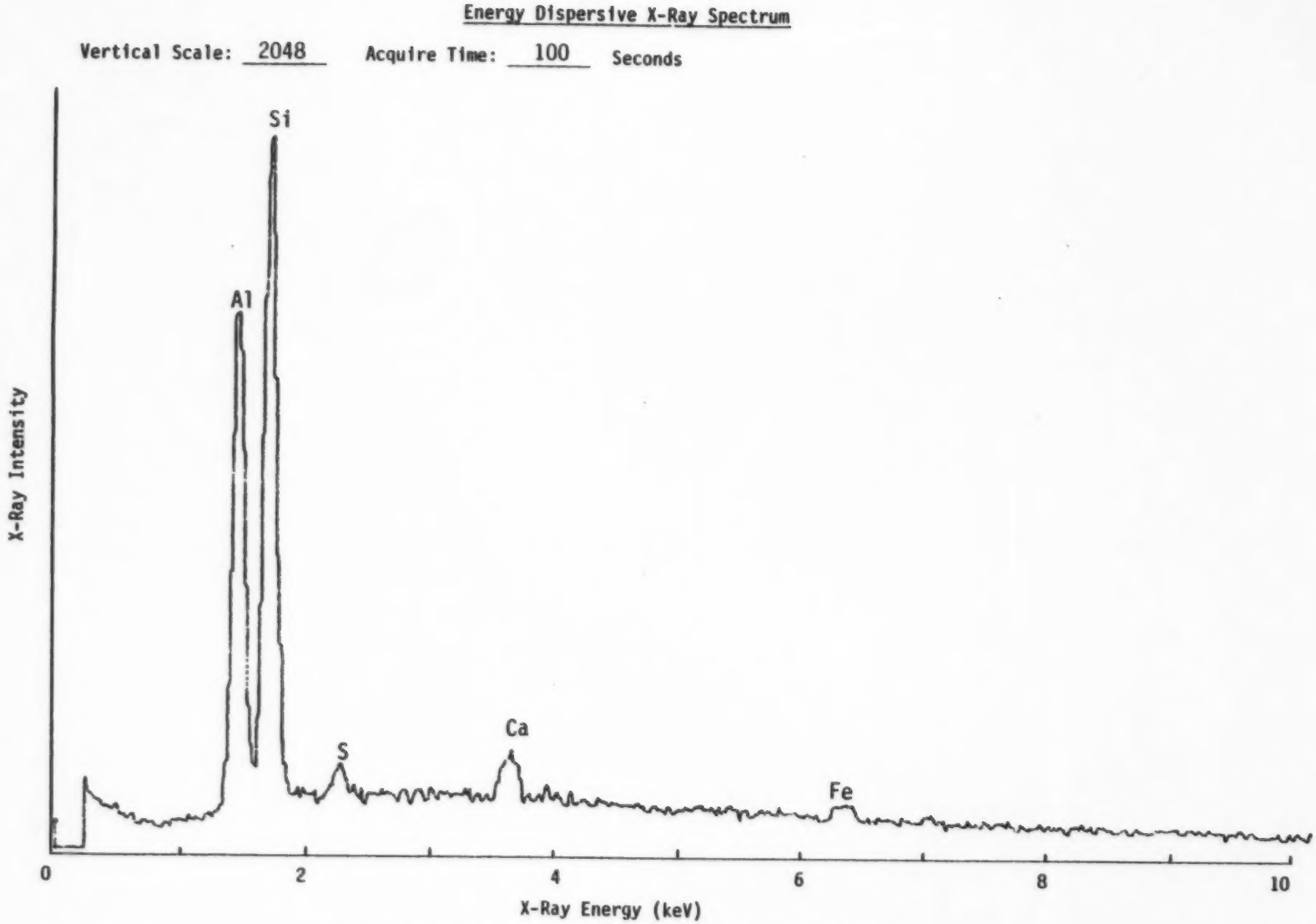

Figure 14. EDXA spectrum of area A as indicated in figure 13.

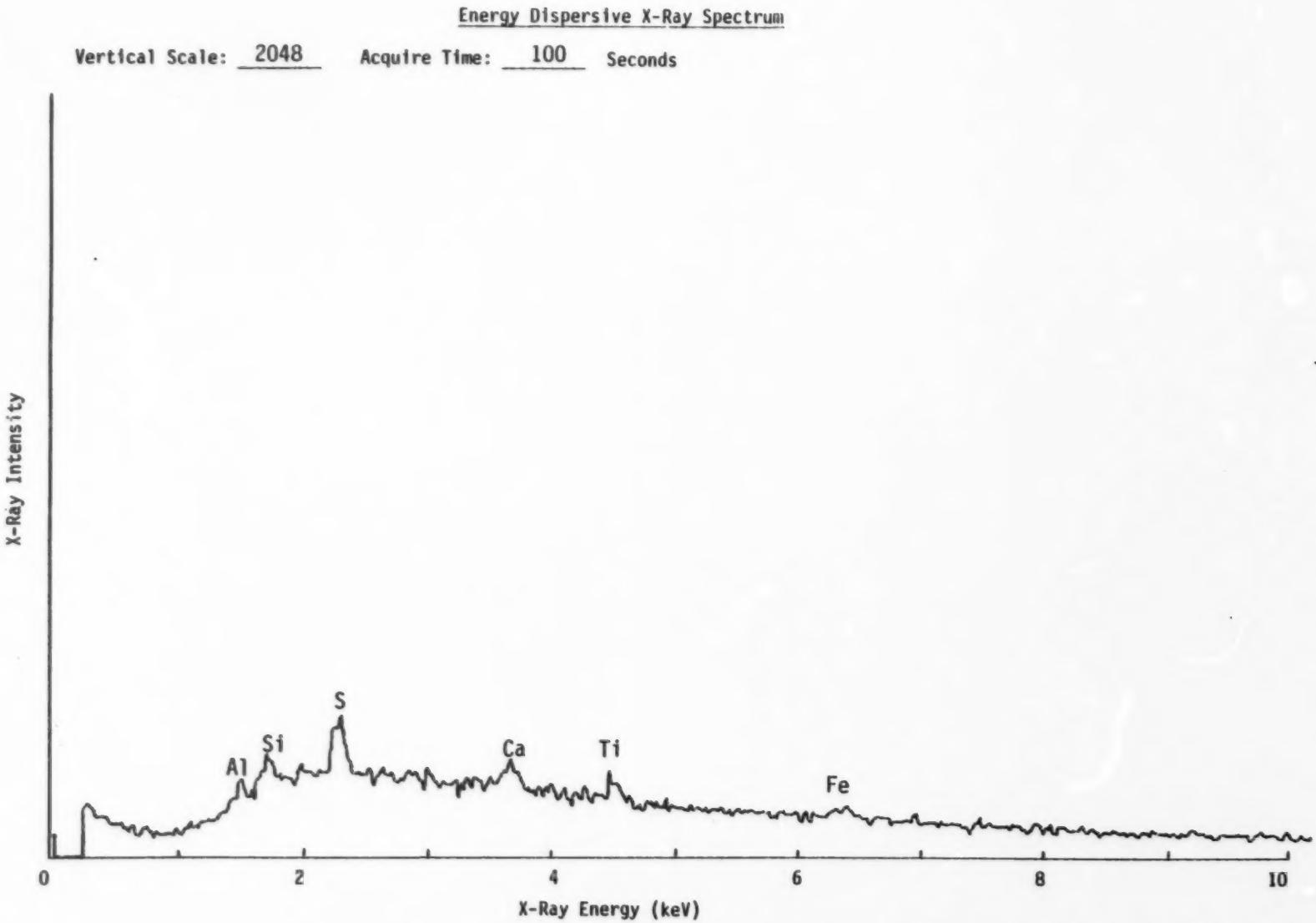

Figure 14a. EDXA spectrum of area B as indicated in figure 13.

Figure 15. Optical micrograph (reflected light, dry objective) of a western low volatile bituminous coal.

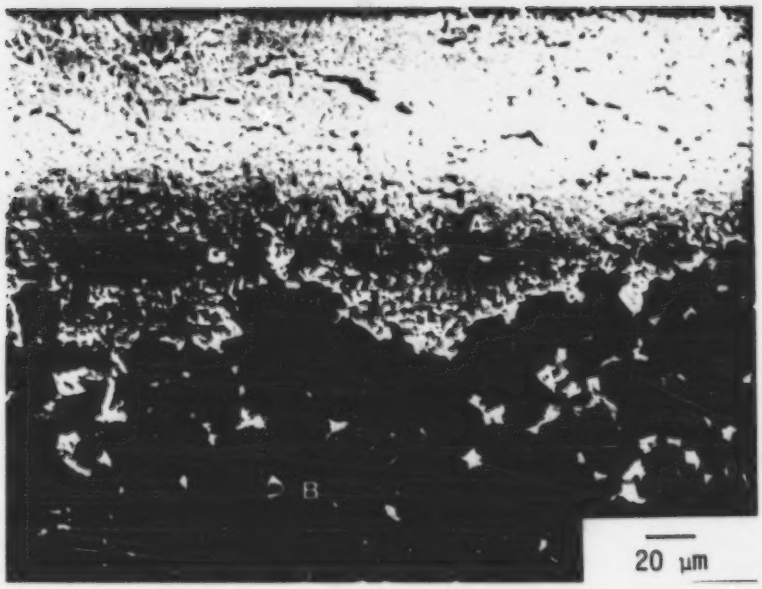

Figure 16. Scanning electron micrograph of a western low volatile bituminous coal. A and B indicate the areas where the EDXA spectra in figures 17 and 18 were acquired.

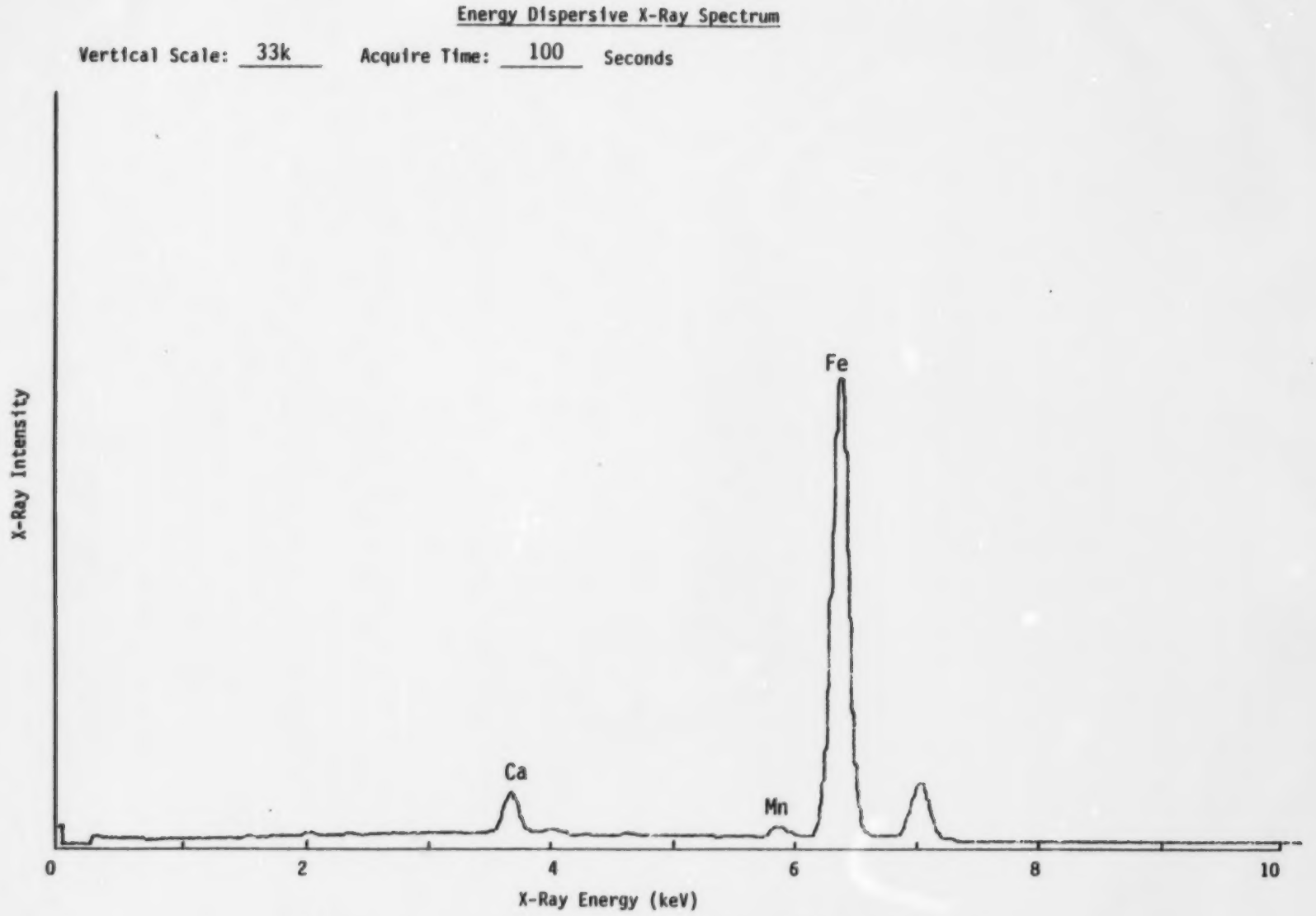

Figure 17. EDXA spectrum of area A as indicated in figure 16.

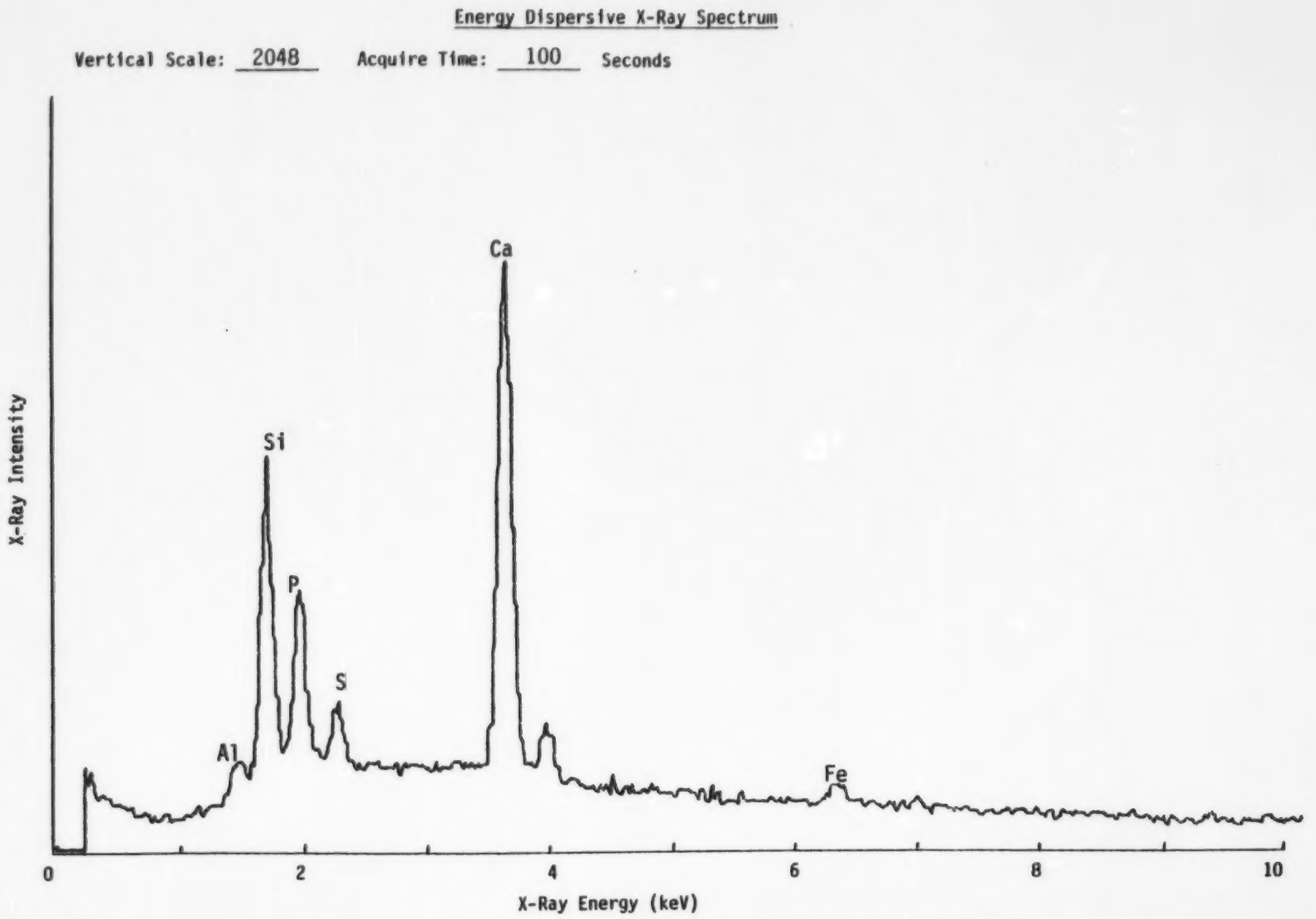

Figure 18. EDXA spectrum of area B as indicated in figure 16.

Figure 19. Optical micrograph (reflected light, dry objective) of a western medium volatile bituminous coal.

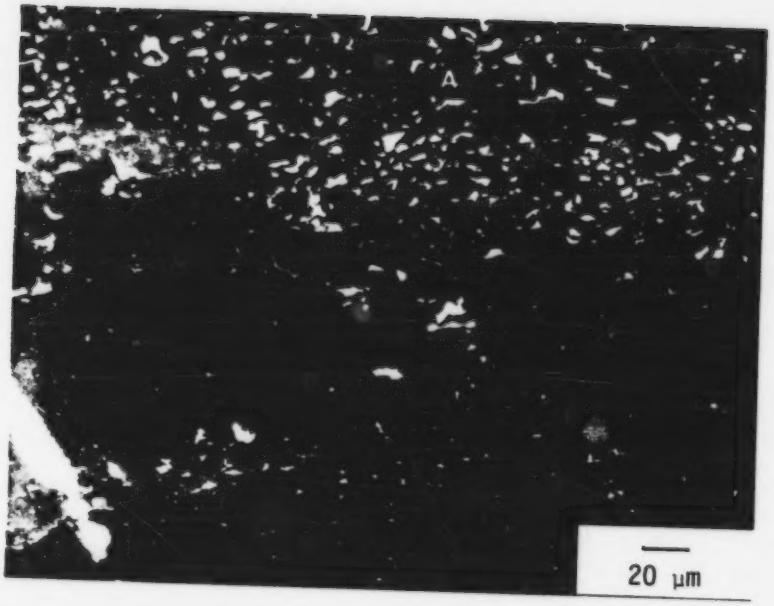

Figure 20. Scanning electron micrograph of a western medium volatile bituminous coal. A indicates the area where the EDXA spectrum in figure 21 was acquired.

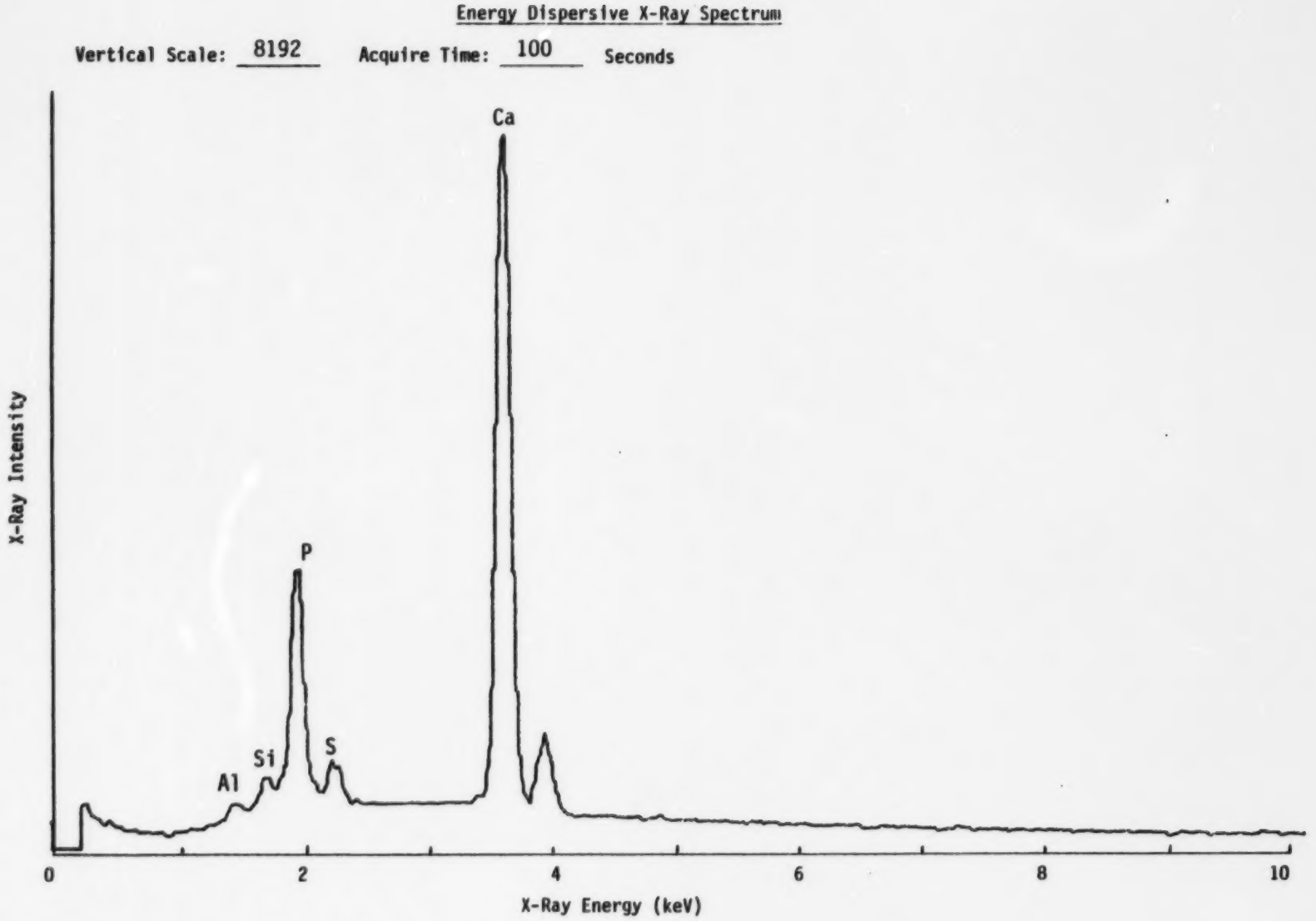

Figure 21. EDXA spectrum of area A as indicated in figure 20.

Figure 22. Optical micrograph (reflected light, dry objective) of a western medium volatile bituminous coal.

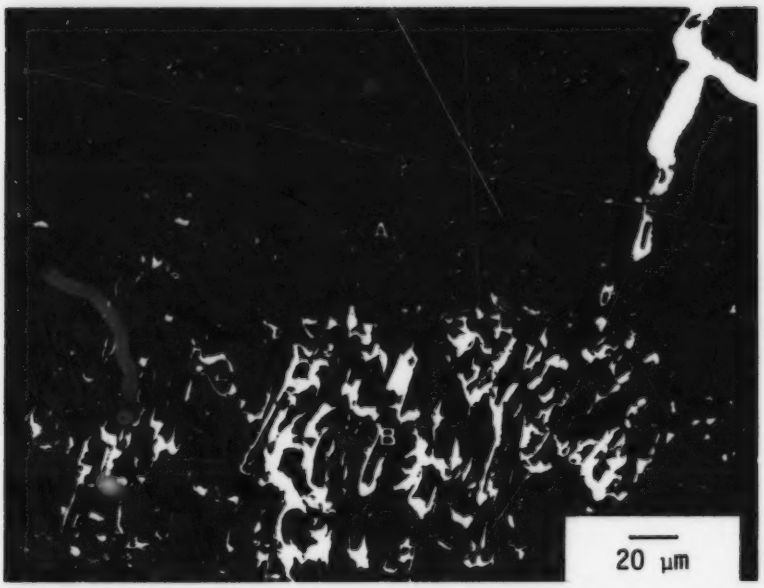

Figure 23. Scanning electron micrograph of a western medium volatile bituminous coal. B and A indicate the areas where the EDXA spectra in figure 24 and 25 were acquired.

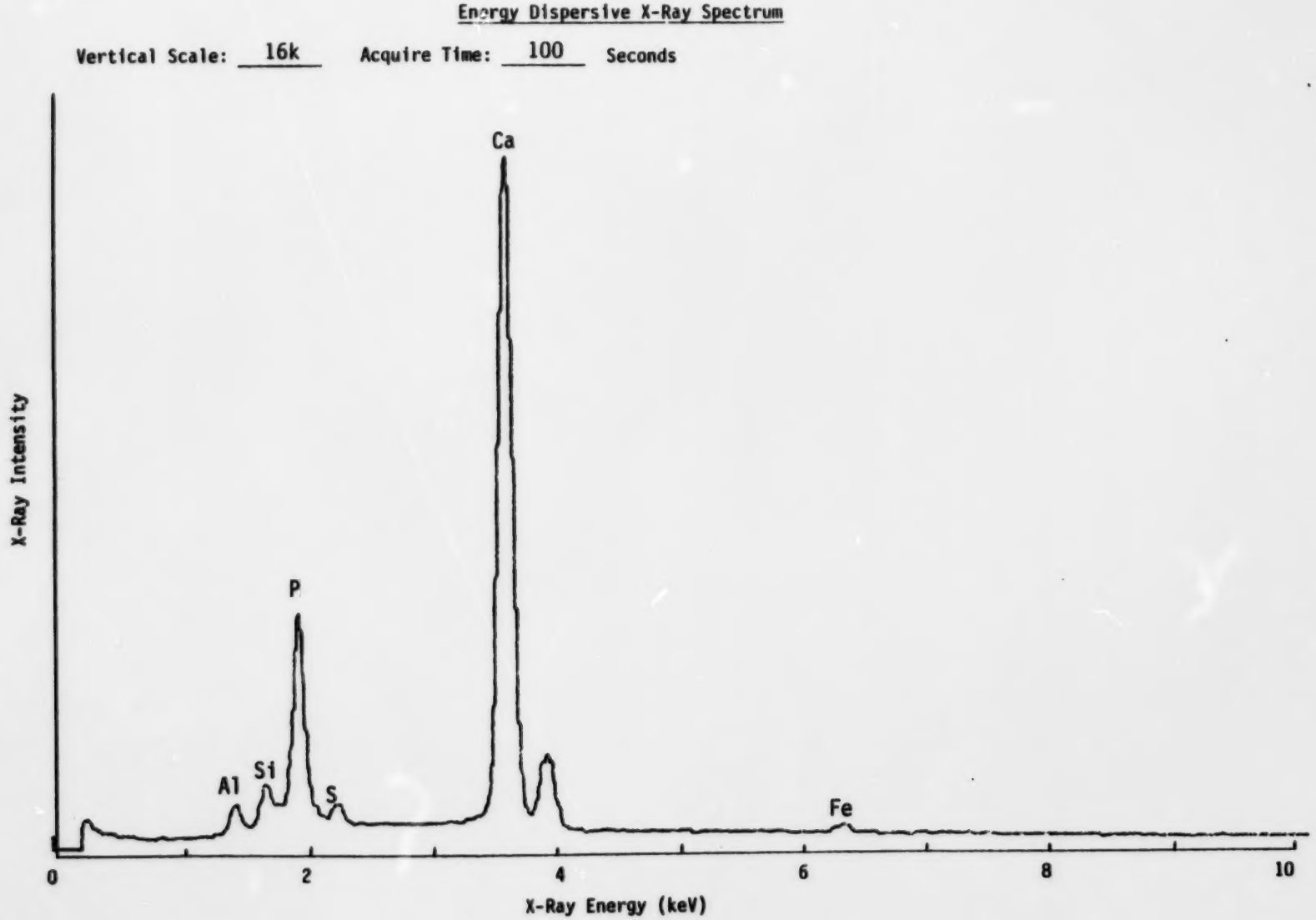

Figure 24. EDXA spectrum of area B as indicated in figure 23.

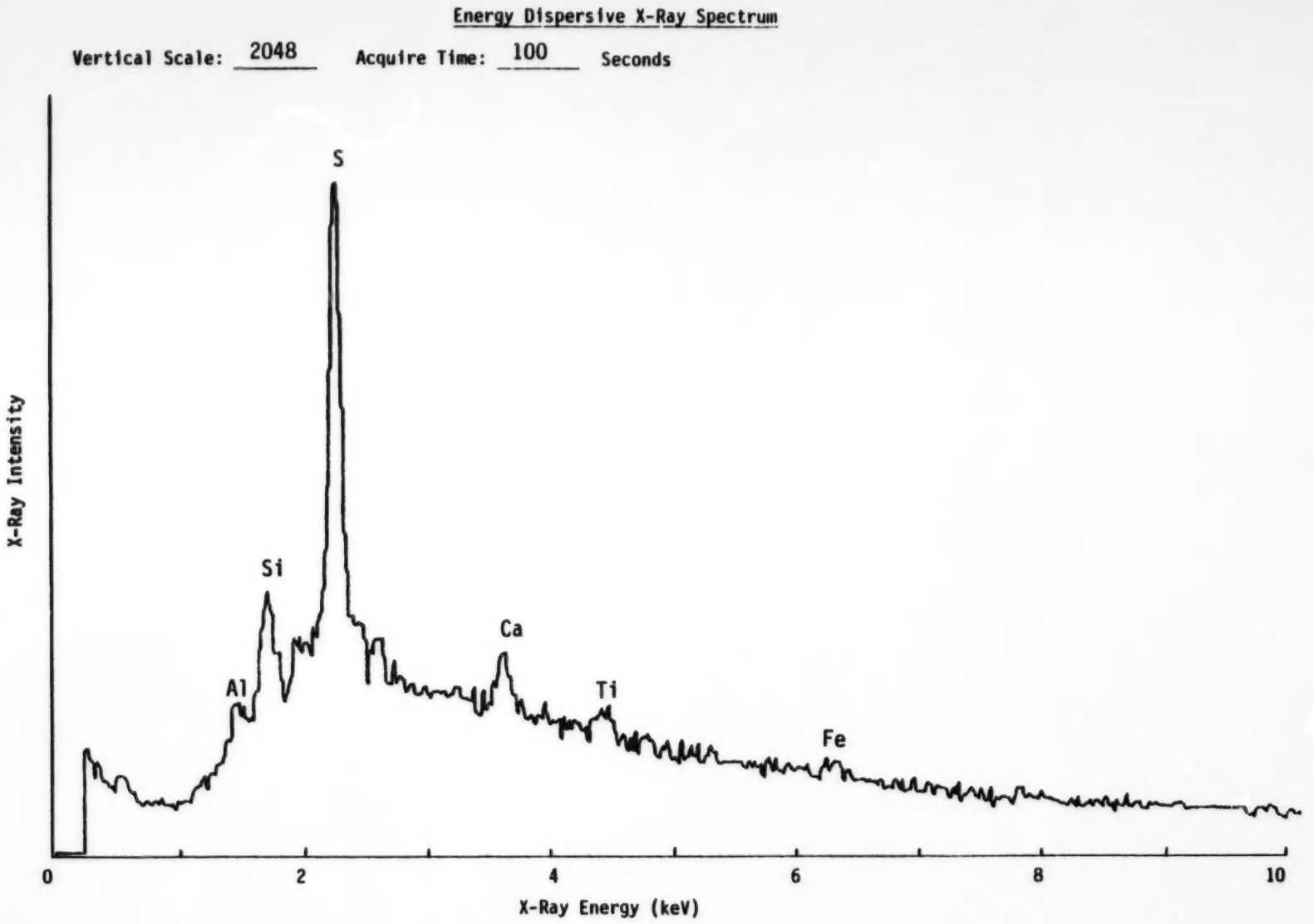

Figure 25. EDXA spectrum of area A as indicated in figure 23.

Figure 26. Optical micrograph (reflected light, dry objective) of a western medium volatile bituminous coal.

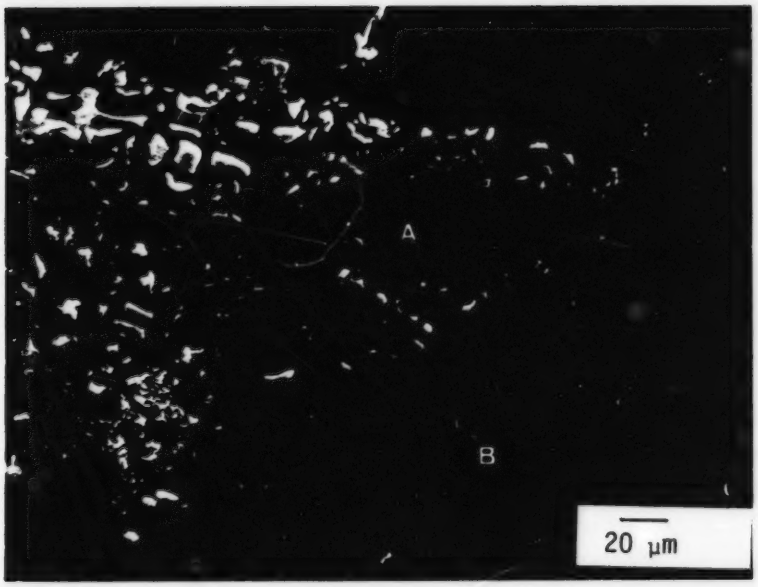

Figure 27. Scanning electron micrograph of a western medium volatile bituminous coal. A and B indicate the areas where the EDXA spectra in figures 28 and 29 were acquired.

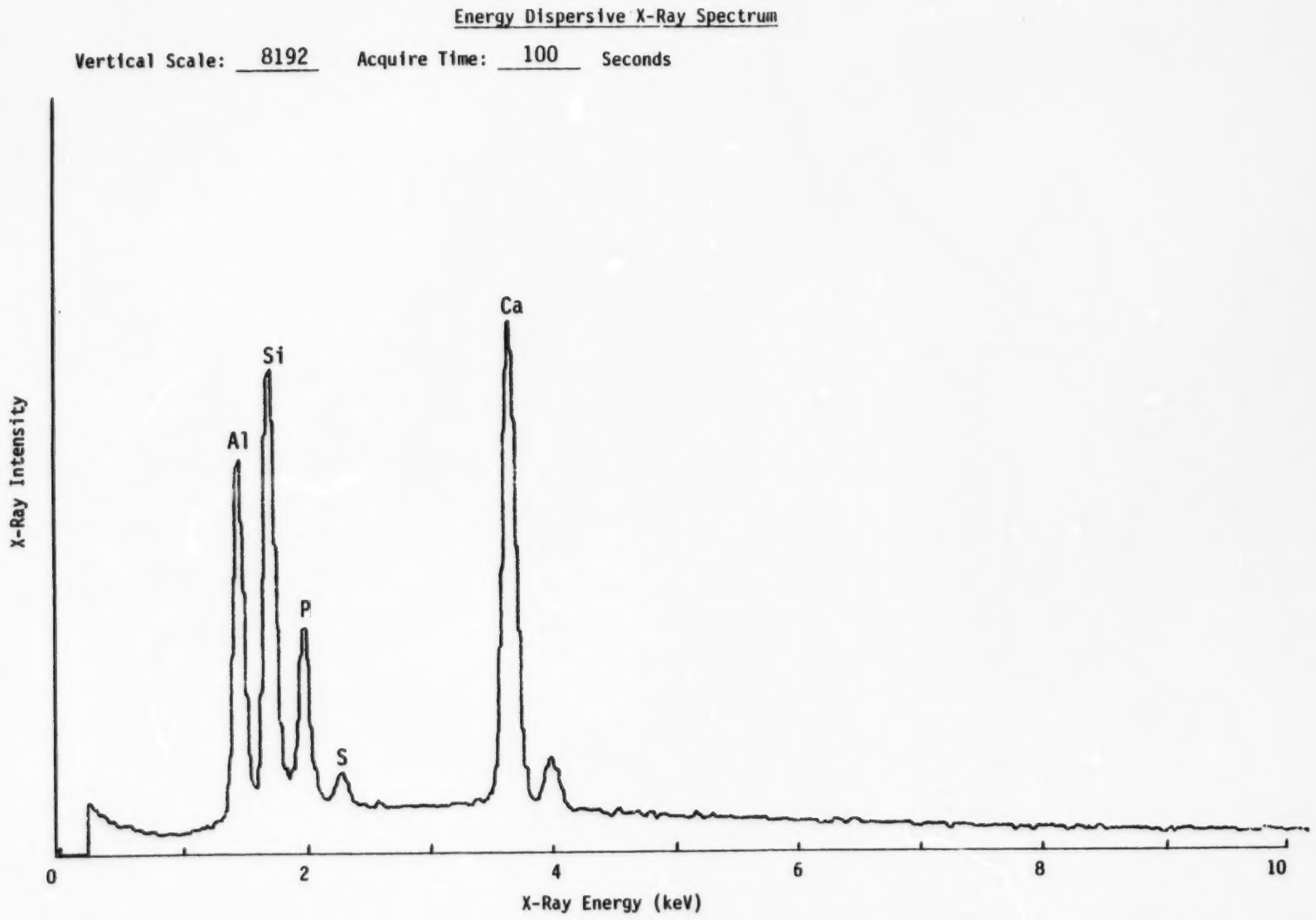

Figure 28. EDXA spectrum of area A as indicated in figure 27.

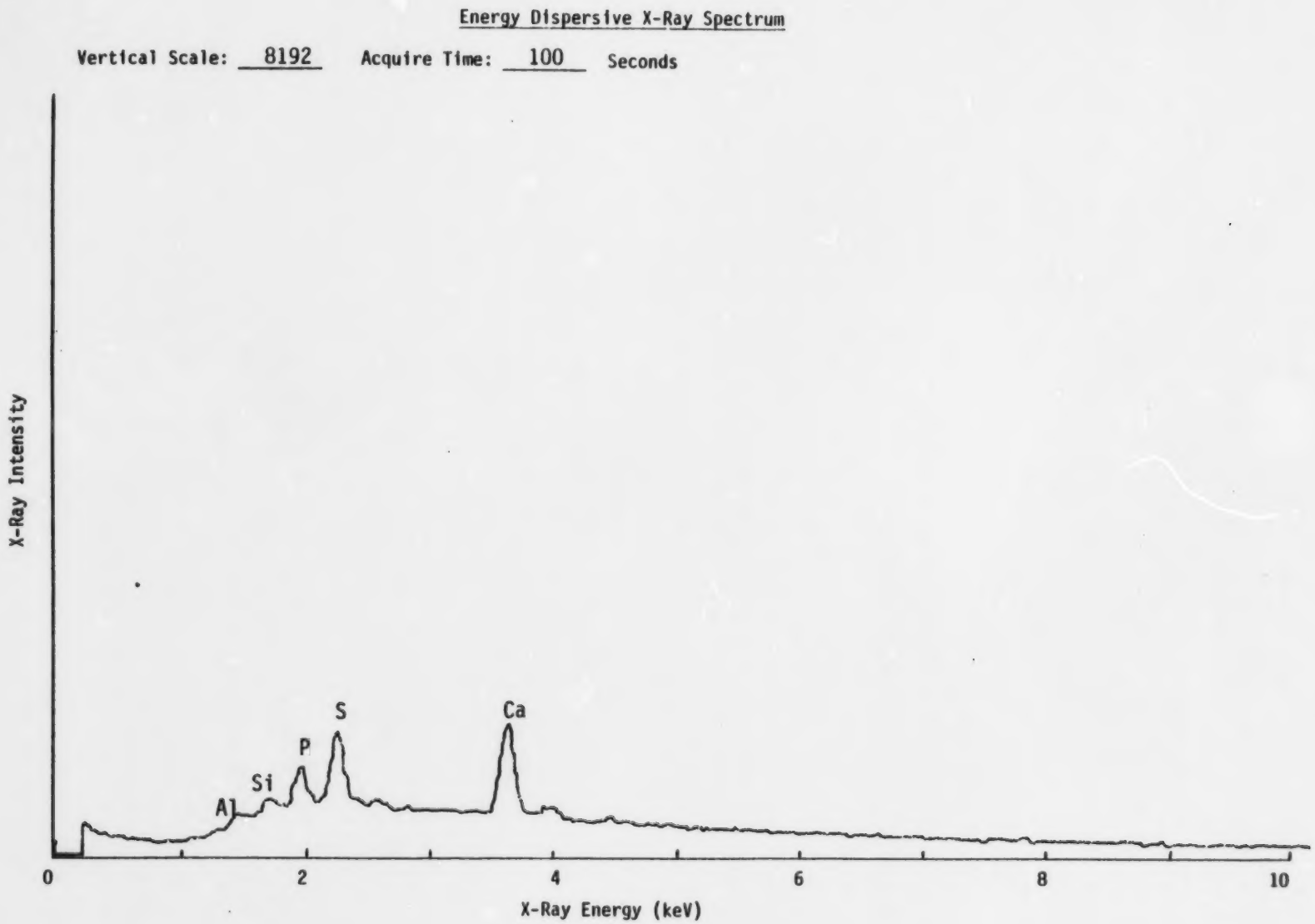

Figure 29. EDXA spectrum of area B as indicated in figure 27.

Figure 30. Optical micrograph (reflected light, dry objective) of a western medium volatile bituminous coal.

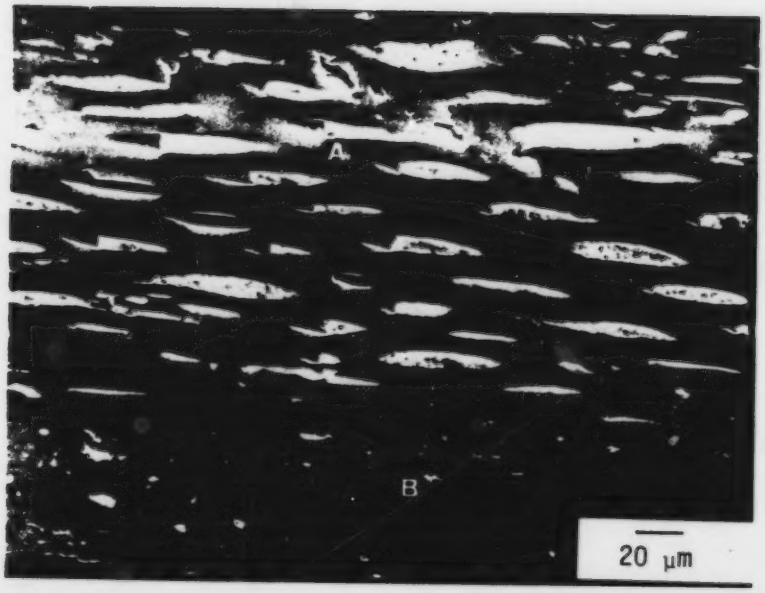

Figure 31. Scanning electron micrograph of a western medium volatile bituminous coal. A and B indicate the areas where the EDXA spectra in figures 32 and 33 were acquired.

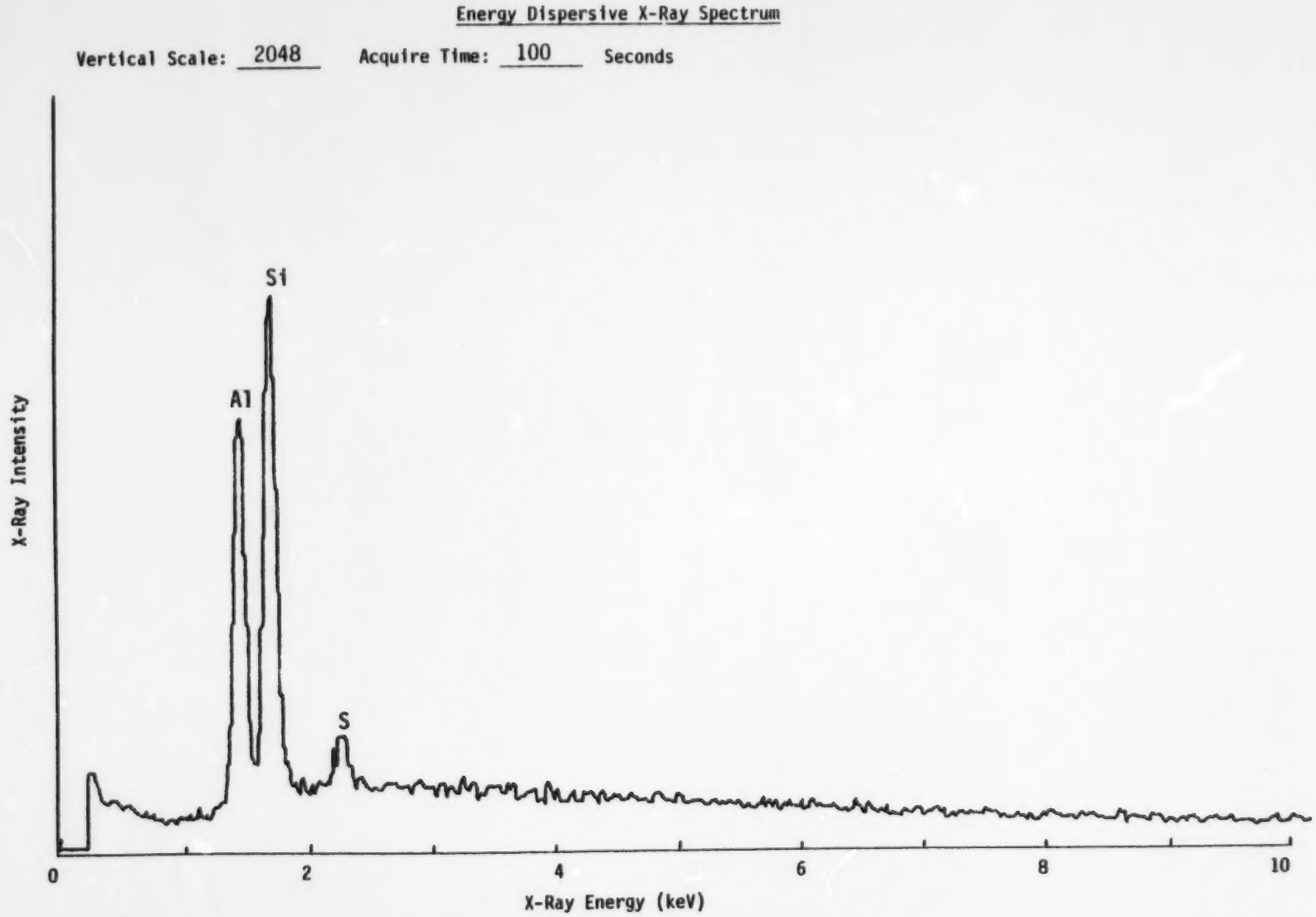

Figure 32. EDXA spectrum of area A as indicated in figure 31.

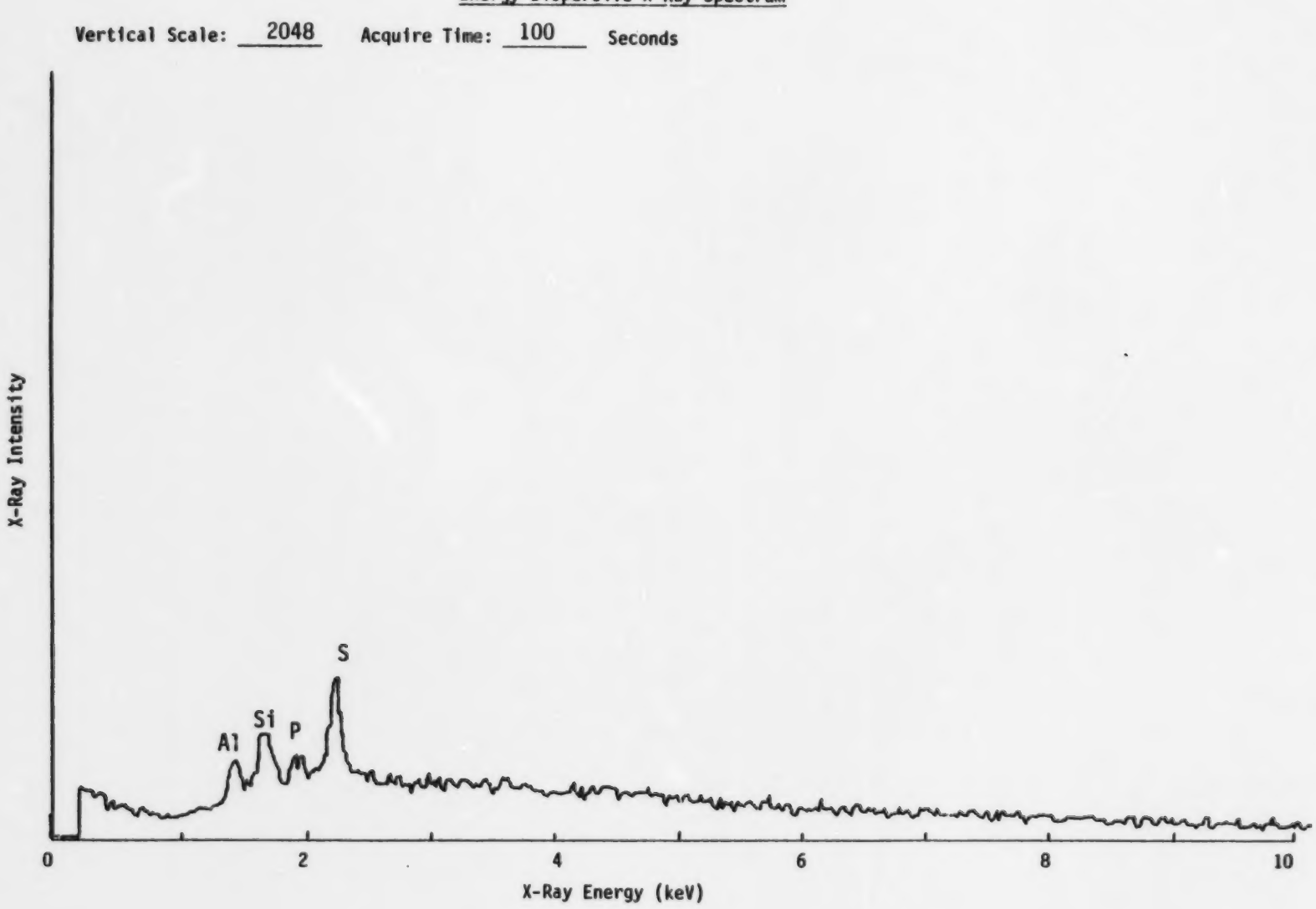

Figure 33. EDXA spectrum of area B as indicated in figure 31.

Figure 34. Optical micrograph (reflected light, dry objective) of an eastern high volatile bituminous coal.

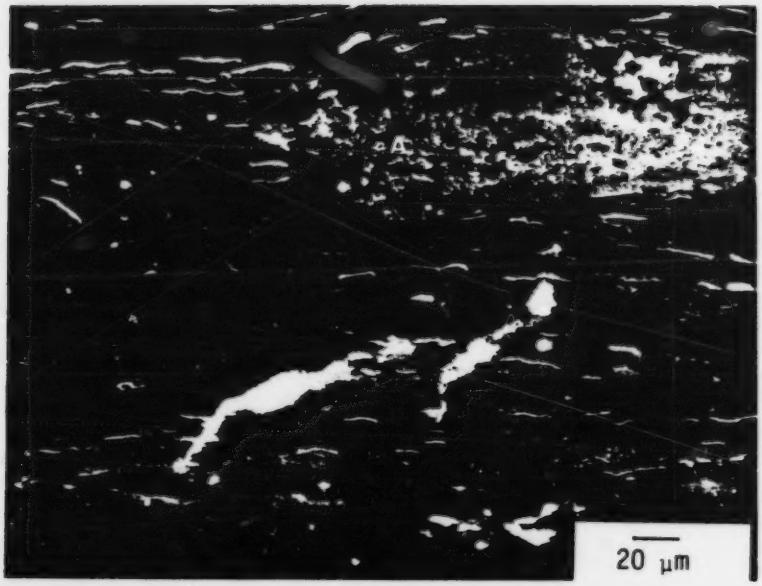

Figure 35. Scanning electron micrograph of an eastern high volatile bituminous coal. A indicates the area where the EDXA spectrum in figure 36 was acquired.

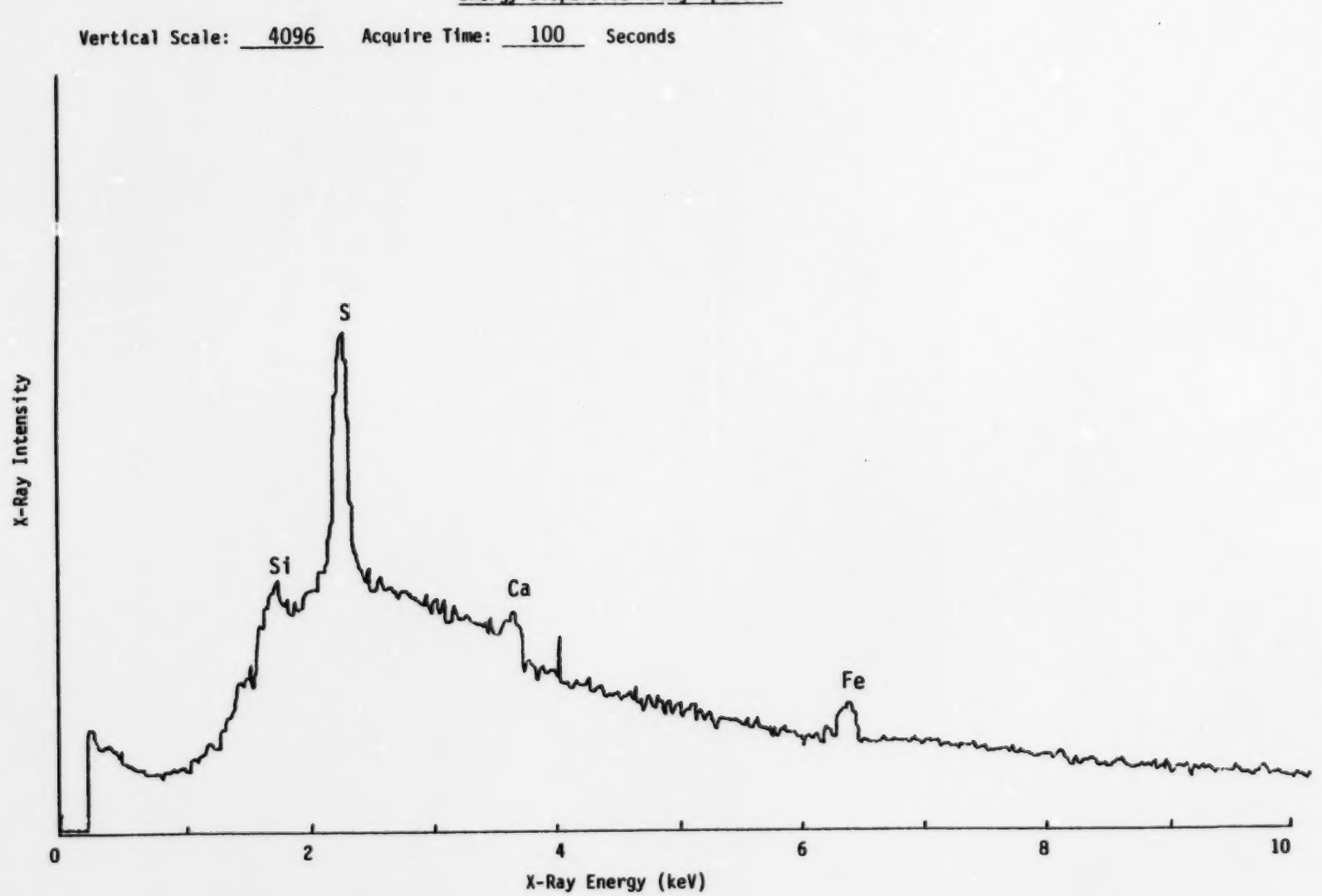

Figure 36. EDXA spectrum of area A as indicated in figure 35.

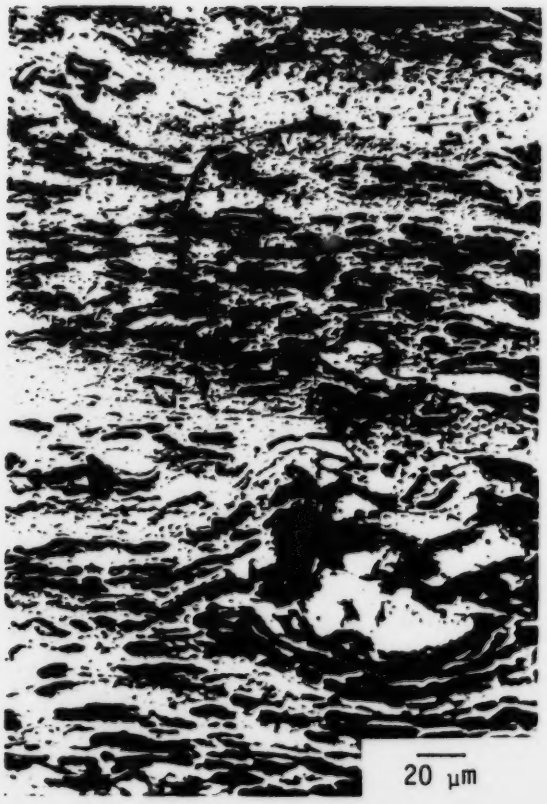

Figure 37. Optical micrograph (reflected light, dry objective) of an eastern high volatile bituminous coal.

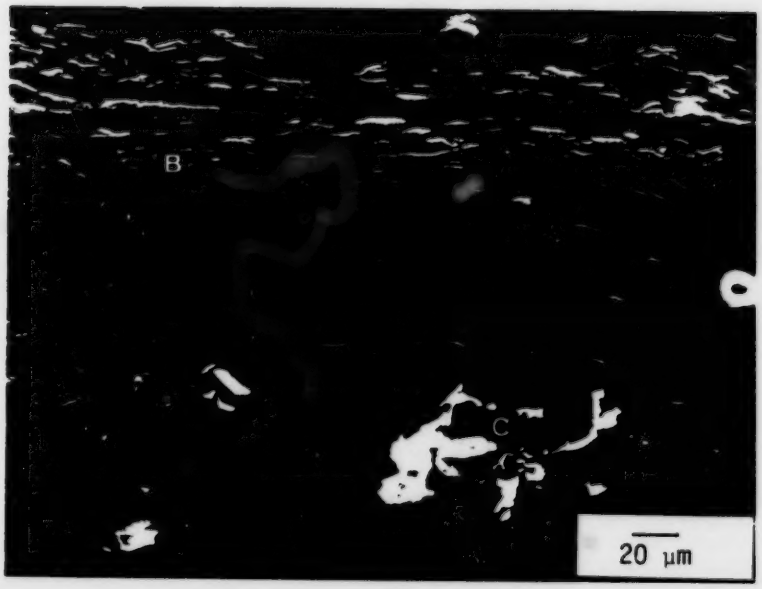

Figure 38. Scanning electron micrograph of an eastern high volatile bituminous coal. B and C indicate the areas where the EDXA spectra in figures 39 and 40 were acquired.

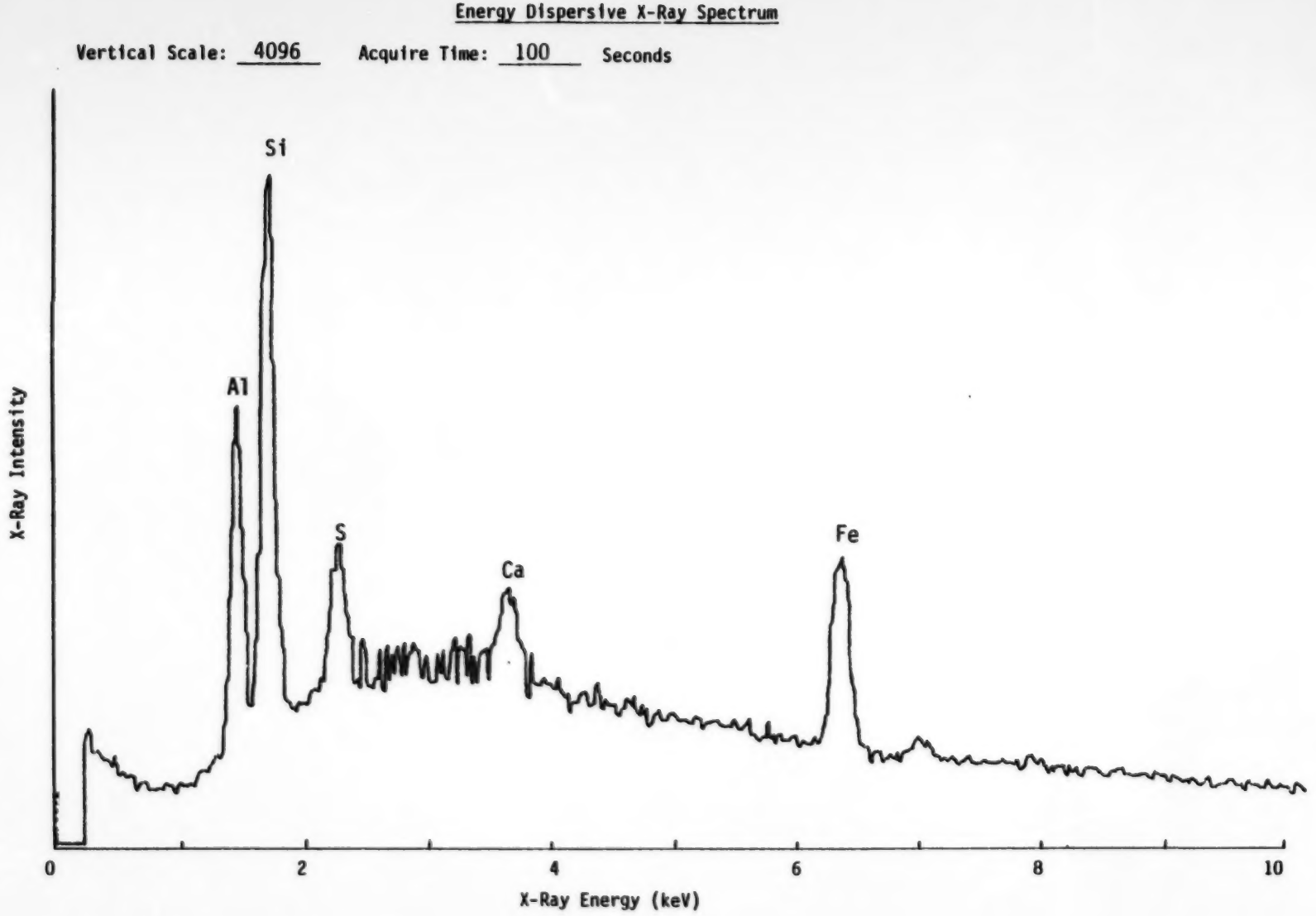

Figure 39. EDXA spectrum of area C as indicated in figure 38.

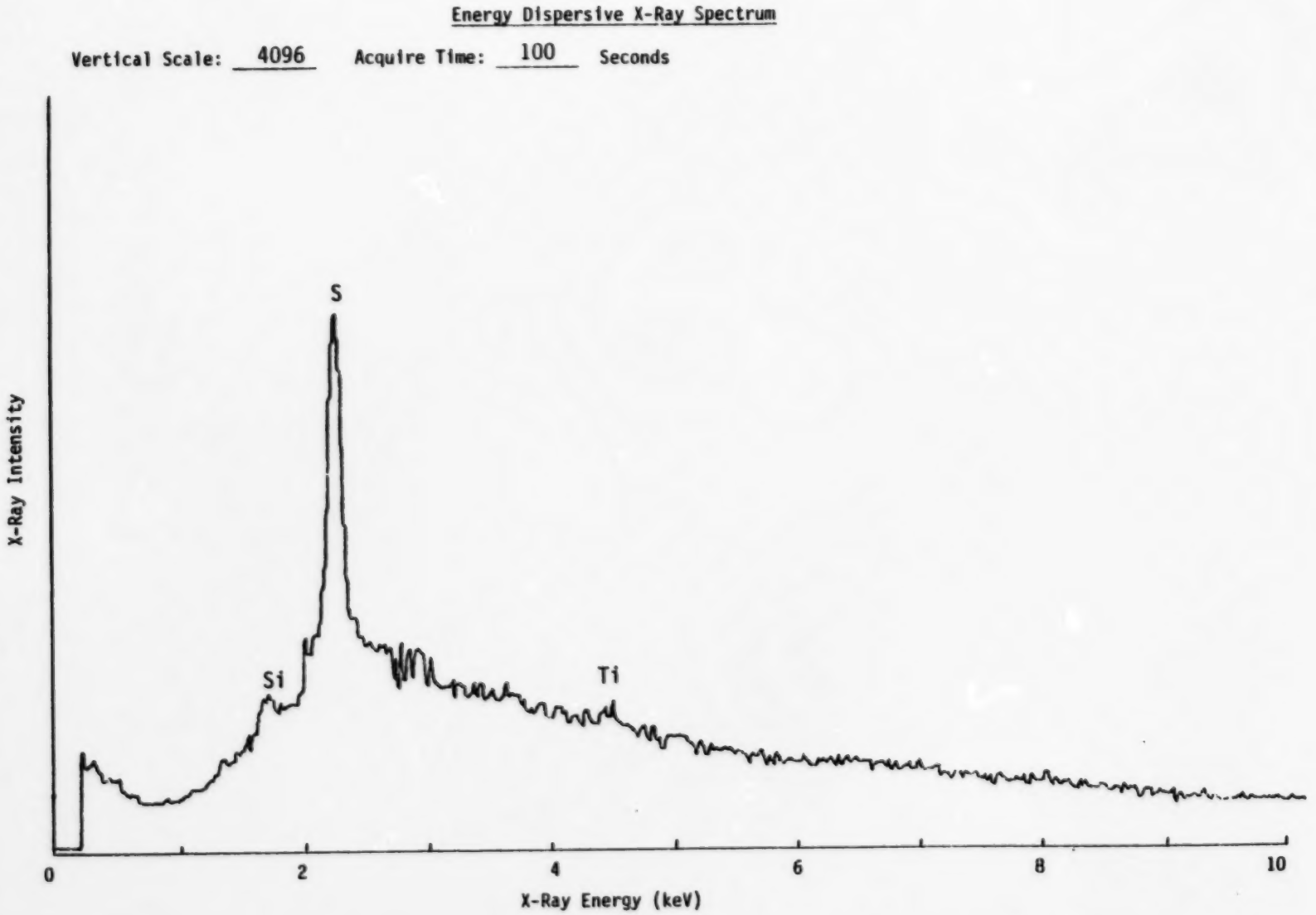

Figure 40. EDXA spectrum of area B as indicated in figure 38.

Figure 41. Optical micrograph (reflected light, dry objective) of an eastern high volatile bituminous coal.

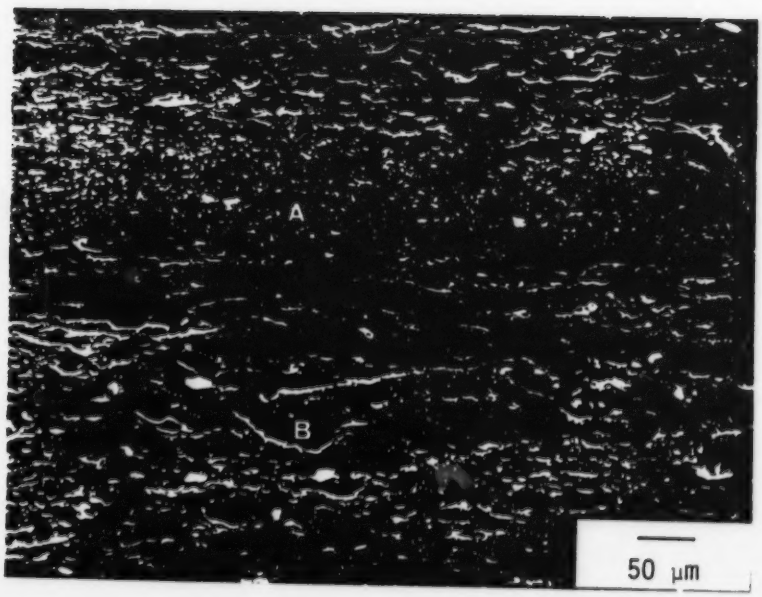

Figure 42. Scanning electron micrograph of an eastern high volatile bituminous coal. A and B indicate the areas where the EDXA spectra in figures 43 and 44 were acquired.

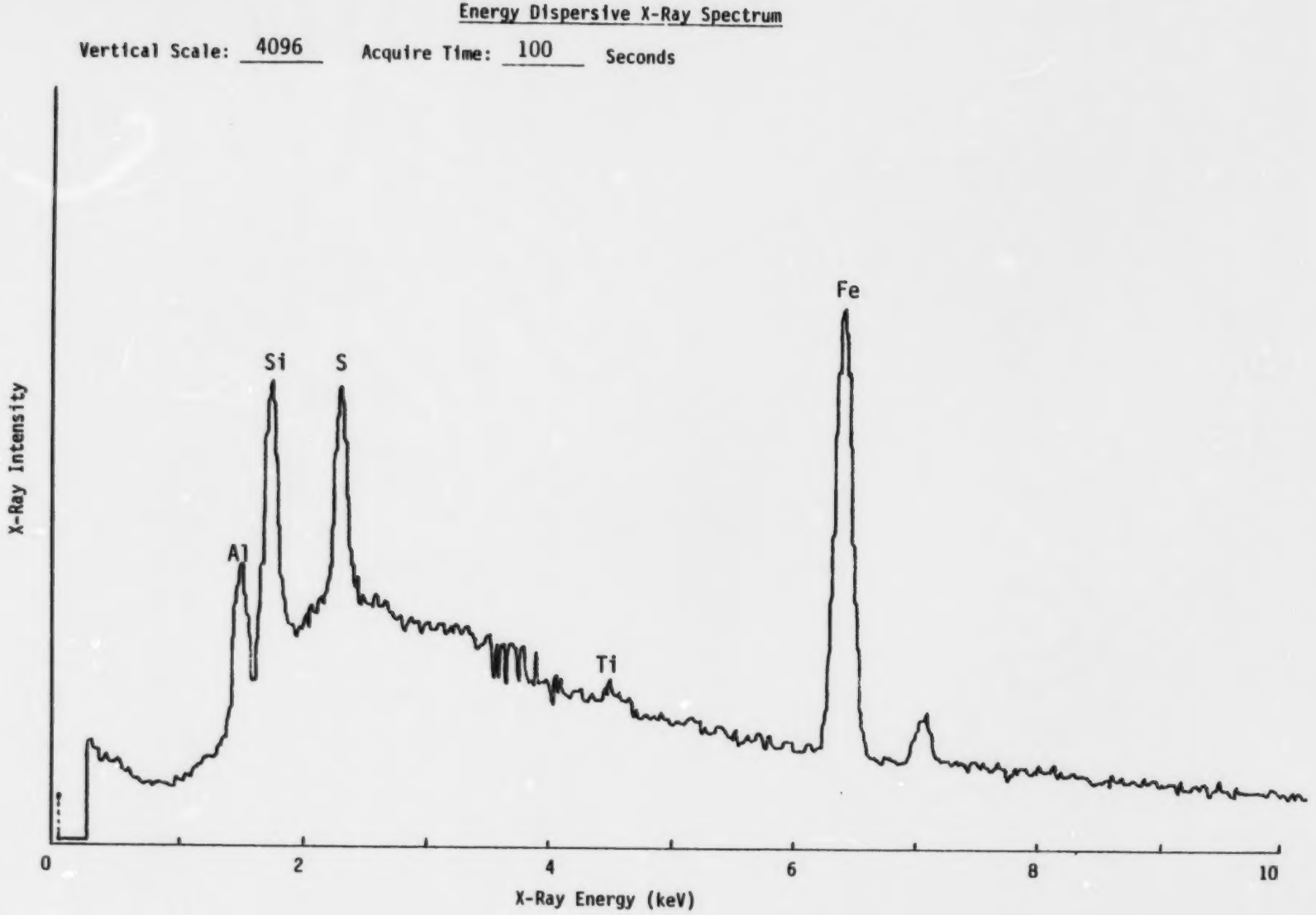

Figure 43. EDXA spectrum of area A as indicated in figure 42.

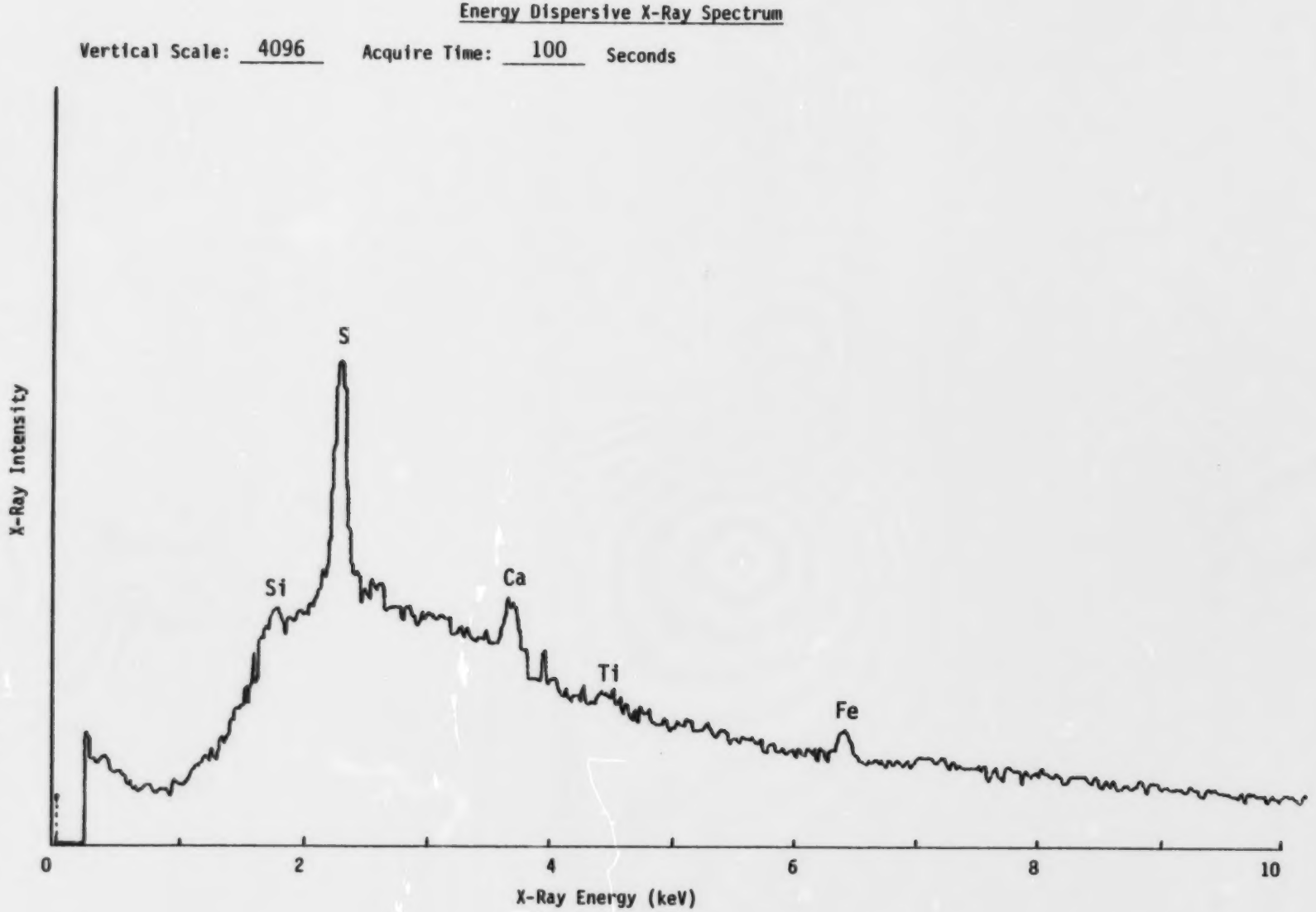

Figure 44. EDXA spectrum of area B as indicated in figure 42.

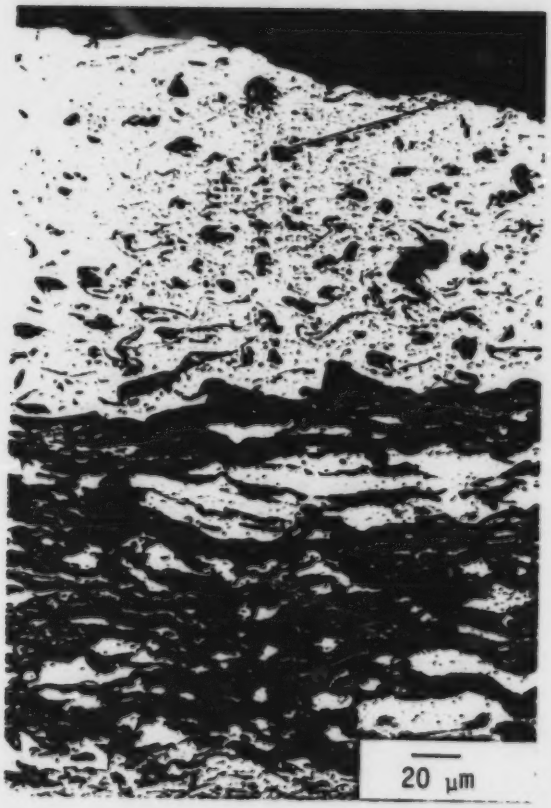

Figure 45. Optical micrograph (reflected light, dry objective) of an eastern high volatile bituminous coal.

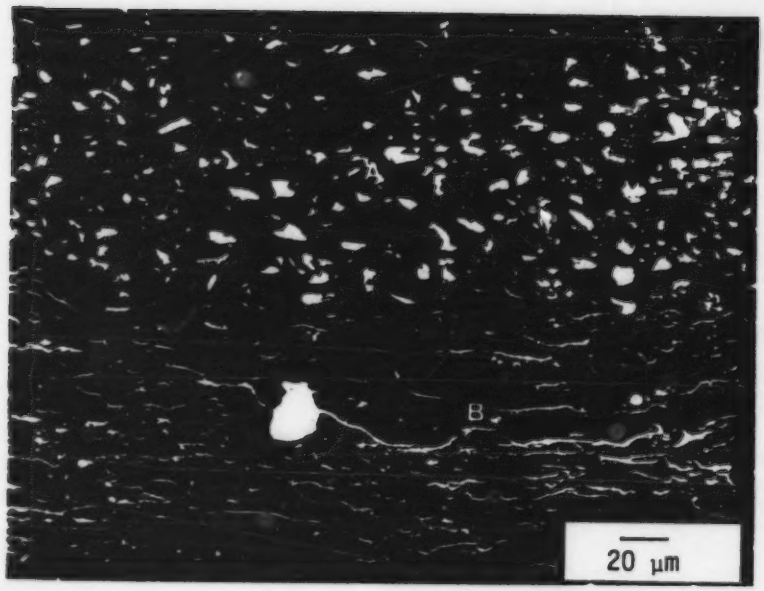

Figure 46. Scanning electron micrograph of an eastern high volatile bituminous coal. A and B indicate the areas where the EDXA spectra in figures 47 and 48 were acquired.

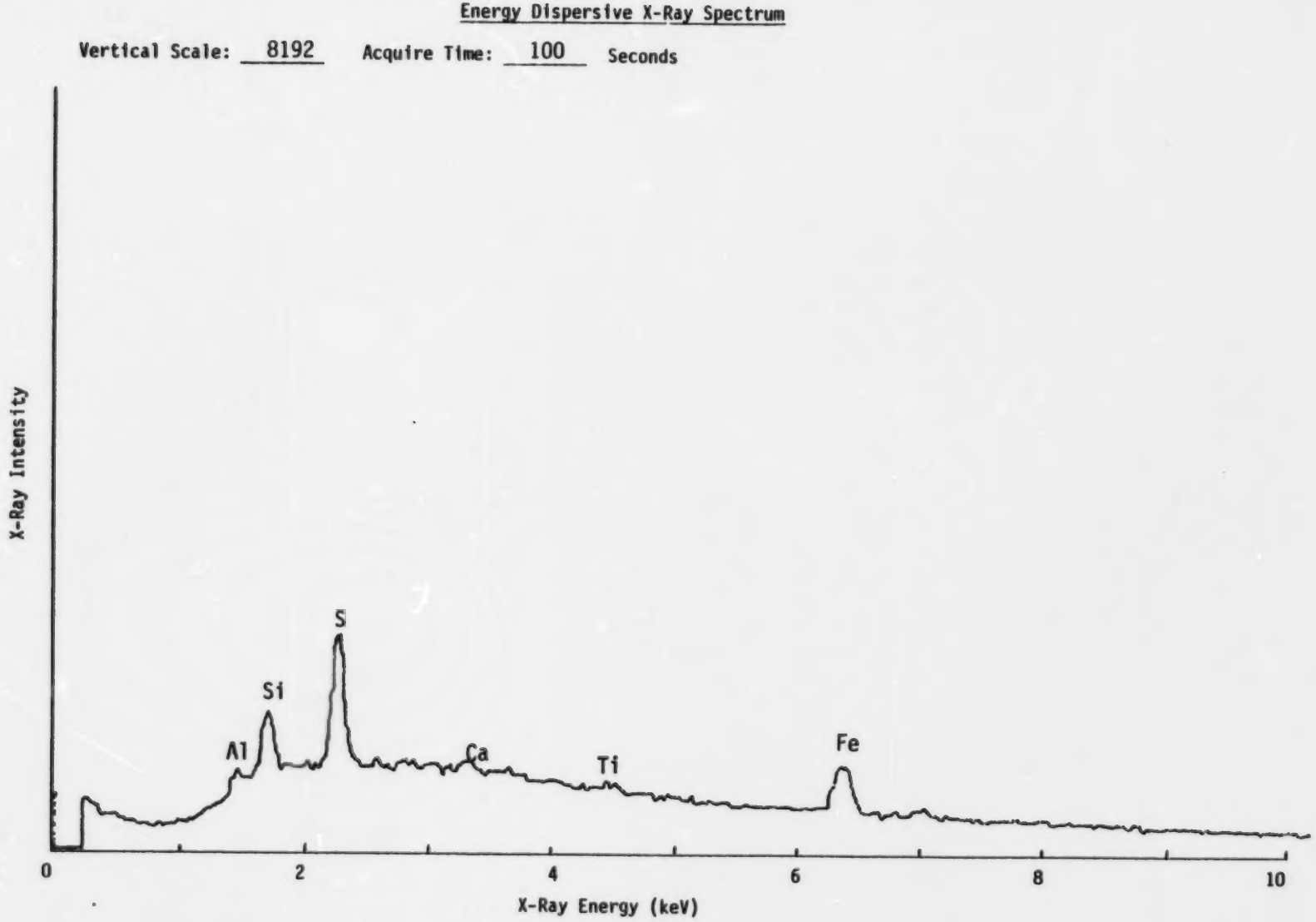

Figure 47. EDXA spectrum of area B as indicated in figure 46.

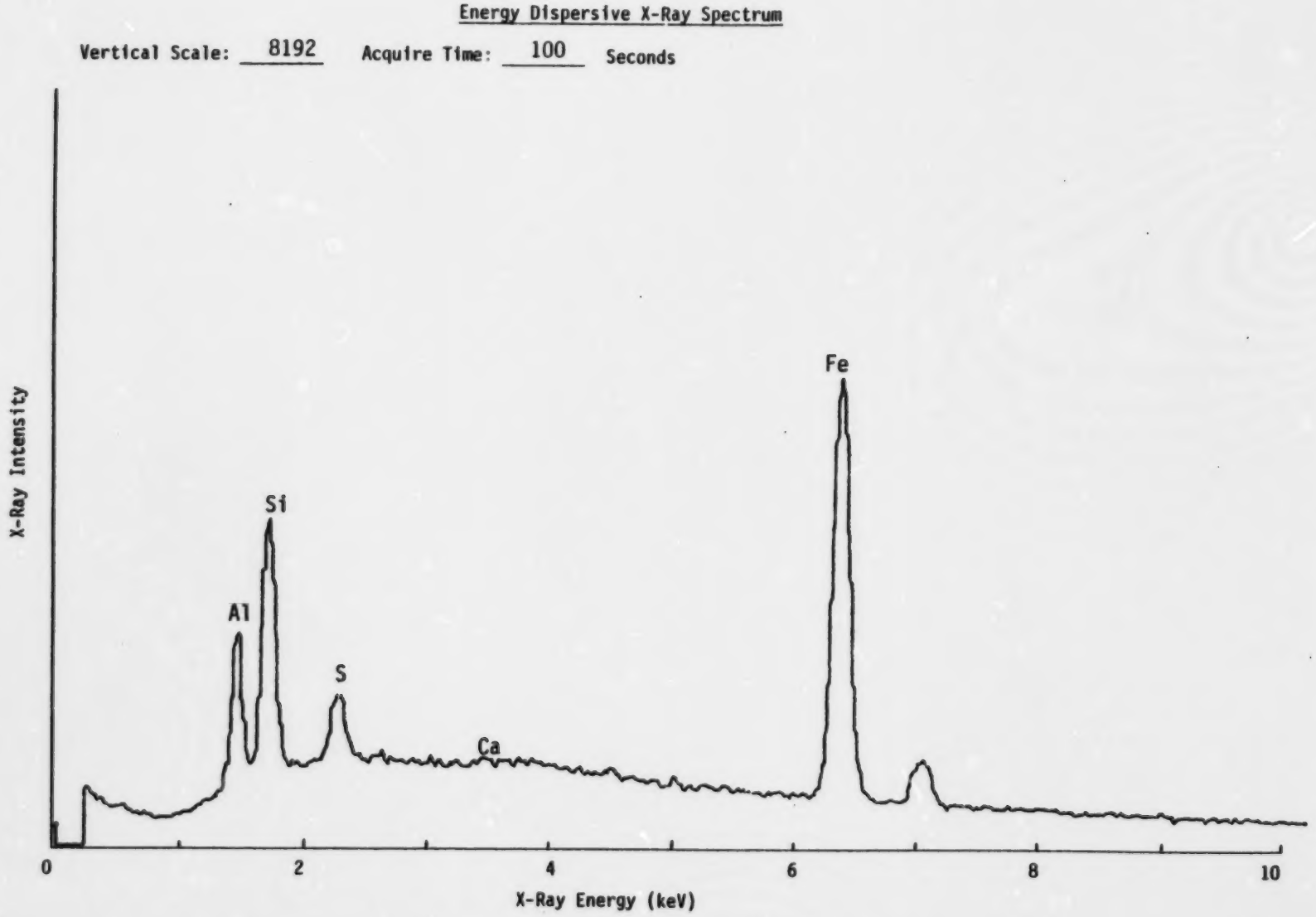

Figure 48. EDXA spectrum of area A as indicated in figure 46.

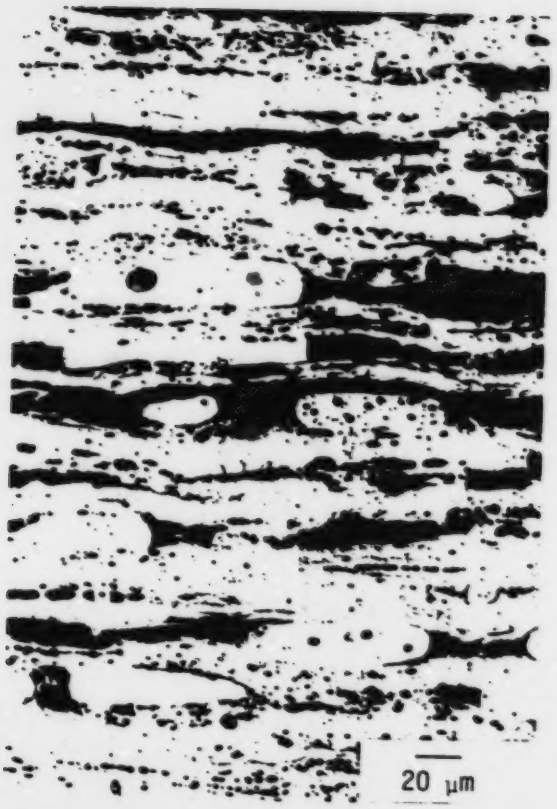

Figure 49. Optical micrograph (reflected light, dry objective) of a Saskatchewan lignite coal.

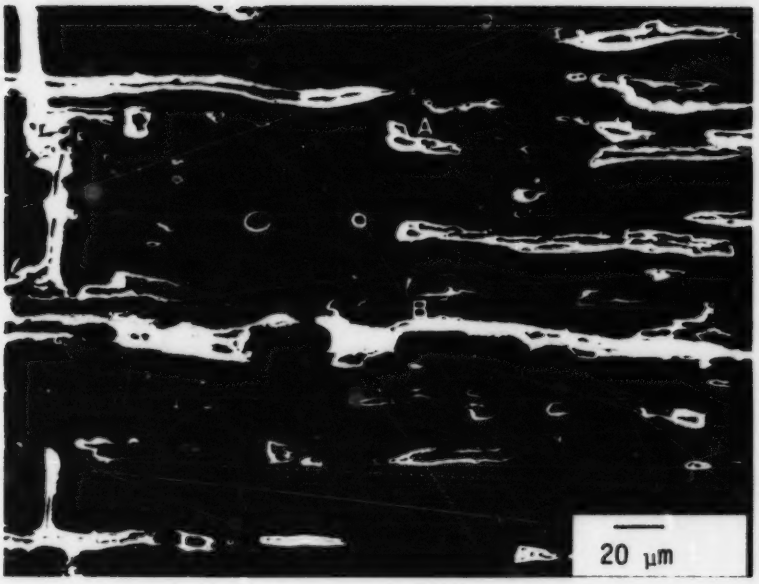

Figure 50. Scanning electron micrograph of a Saskatchewan lignite coal. A indicates the area where the EDXA spectrum in figure 51 was acquired.

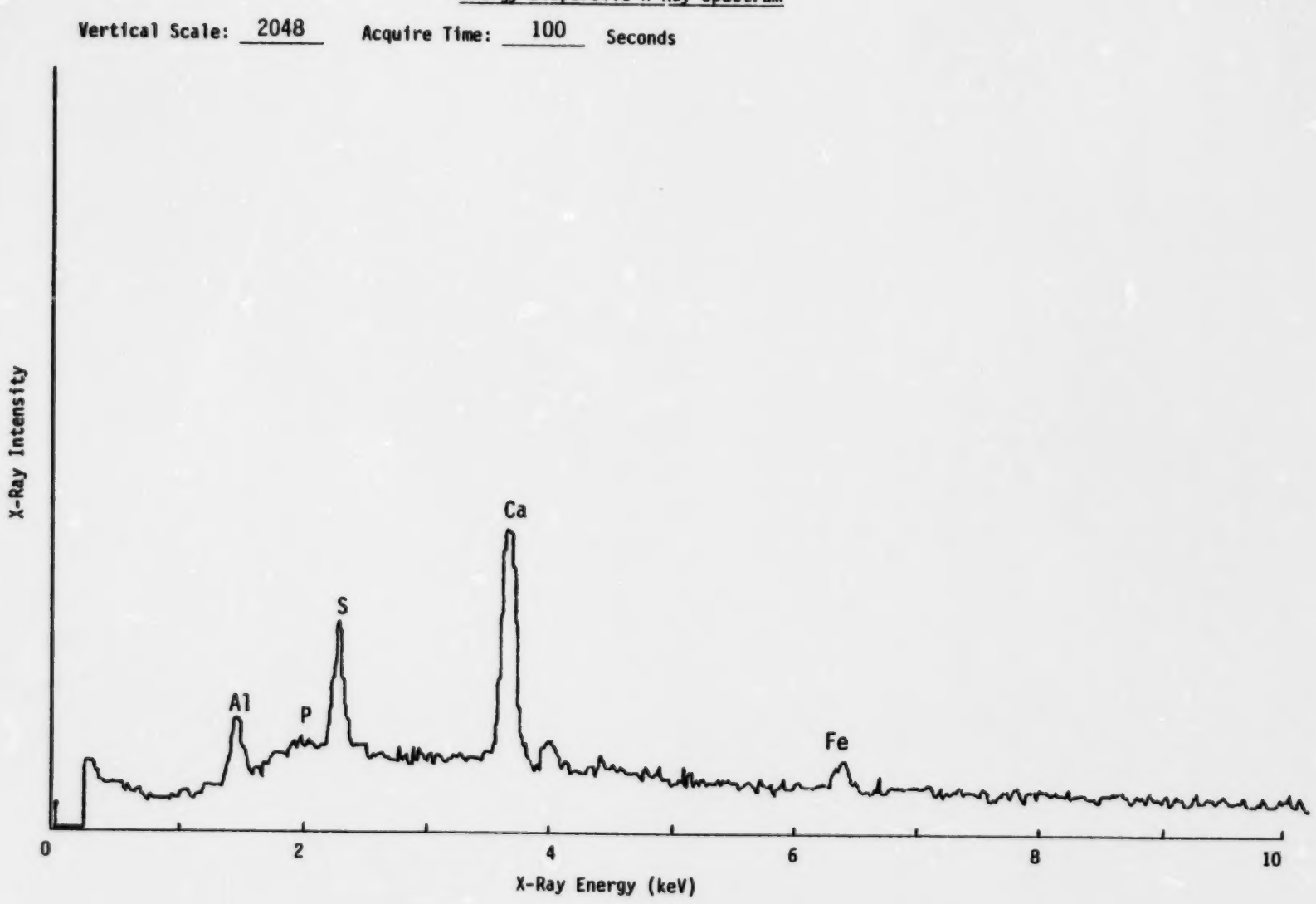

Figure 51. EDXA spectrum of area A as indicated in figure 50.

Figure 52.

Figure 53.

Figures 52 and 53. Transmission electron micrographs of an ion-milled sample of eastern high volatile bituminous coal illustrating pores in the size range of 30 nm. to 50 nm.

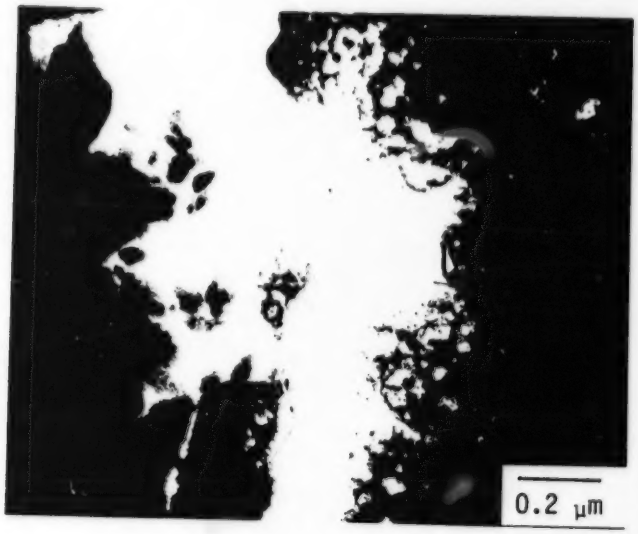

Figure 54.

Figure 55.

Figures 54 and 55. Transmission electron micrographs of an ion-milled sample of western medium volatile bituminous coal, illustrating interconnecting pore channels on the left side.

Figure 56.

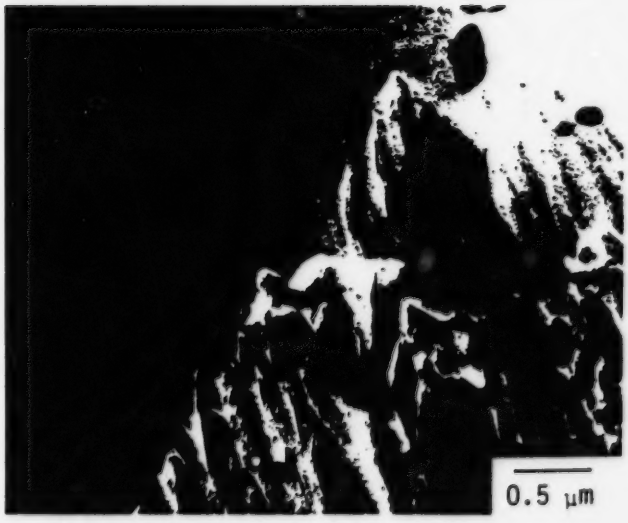

Figure 57.

Figures 56 and 57. Transmission electron micrographs of ion-milled western low volatile bituminous coal coated with small globules of copper resulting from the ion-milling of the copper sample support ring.

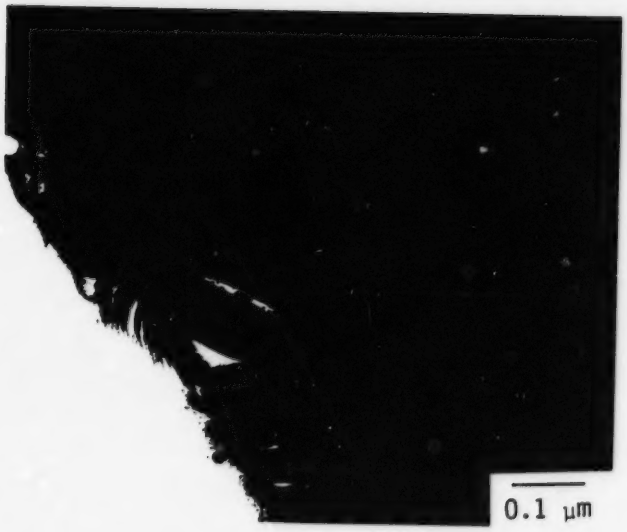

Figure 58. Transmission electron micrograph of an ion-milled sample of western low volatile bituminous coal illustrating fine detail which may be pores in the size range 10 nm to 20 nm.

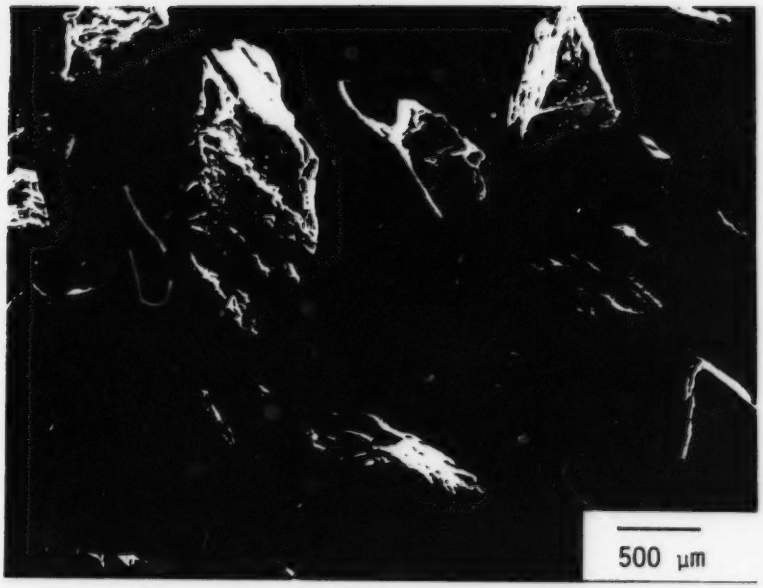

Figure 59. Scanning electron micrograph of the oxidized bituminous coal sample.

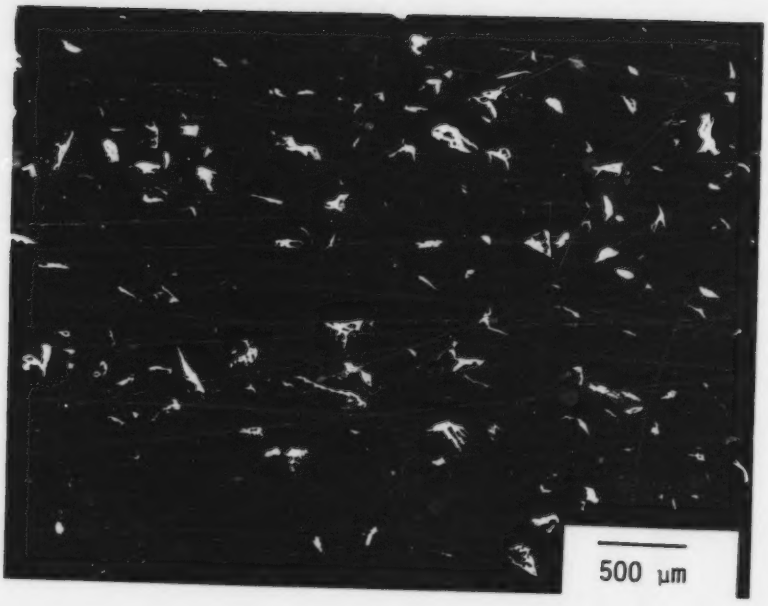

Figure 60. Scanning electron micrograph of the oxidized sub-bituminous coal sample.

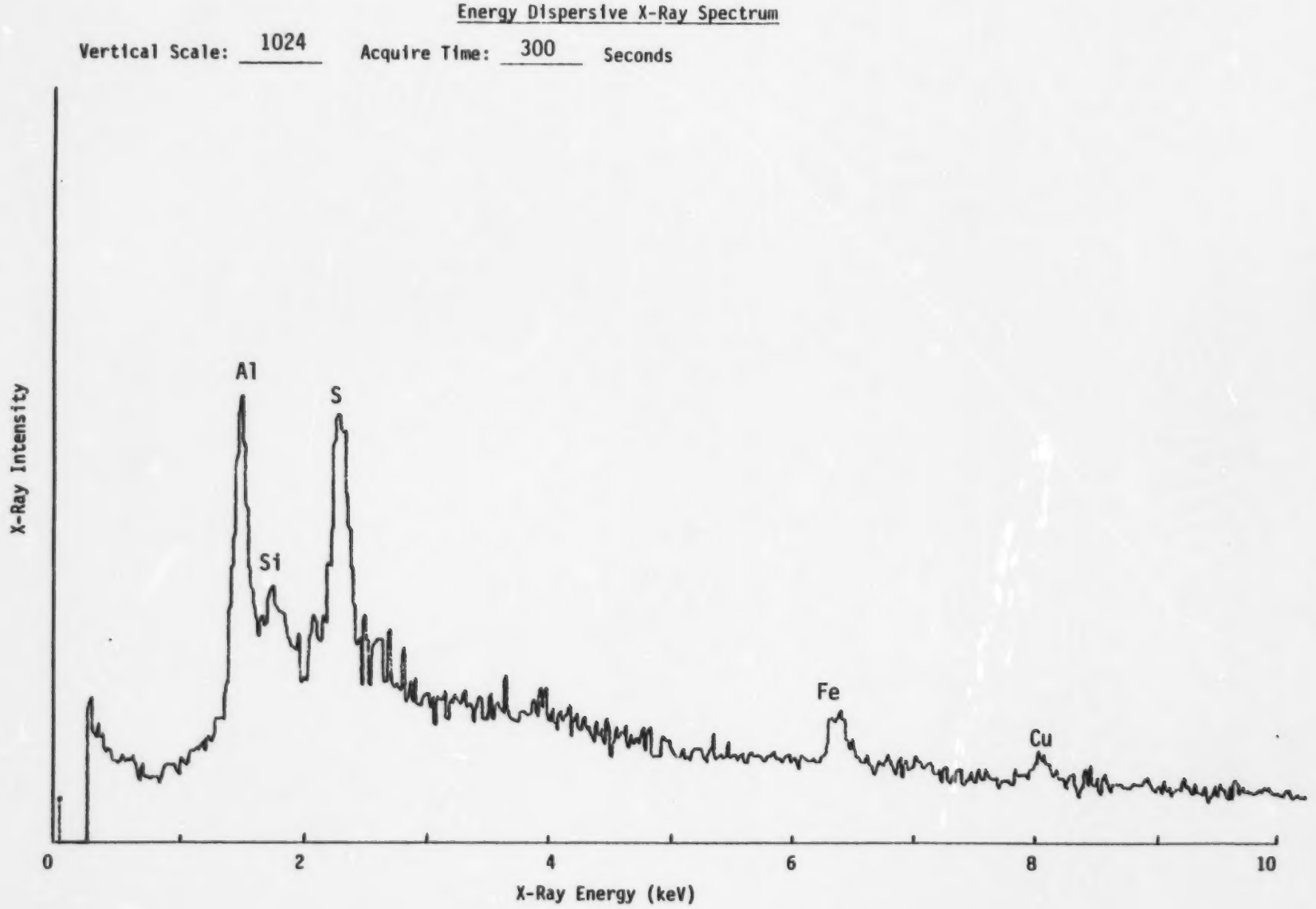

Figure 61. EDXA spectrum of the oxidized bituminous coal sample shown in figure 61.

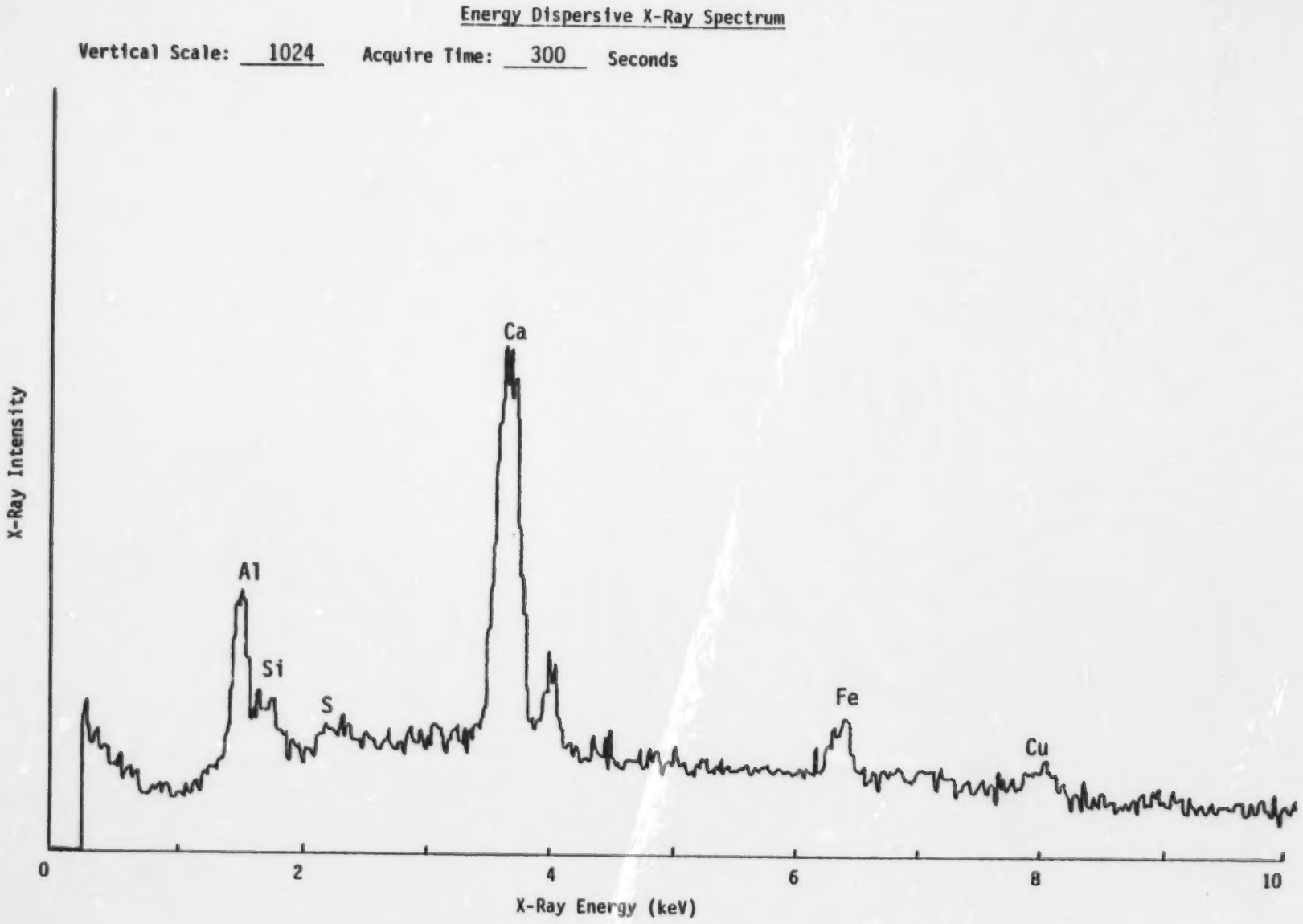

Figure 62. EDXA spectrum of the oxidized sub-bituminous coal shown in figure 59.

Figure 63. Transmission electron micrograph of an ion-milled sample of epoxy mounted oxidized bituminous coal.

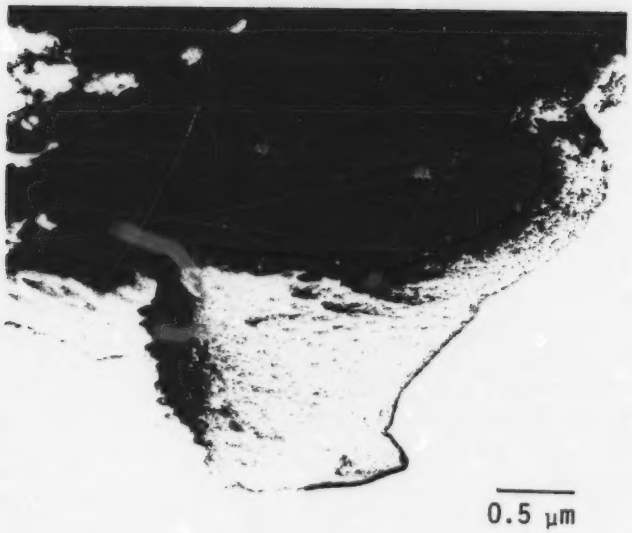

Figure 64. Transmission electron micrograph of an ion-milled sample of Saskatchewan lignite illustrating the ripples produced by the ion-milling process.

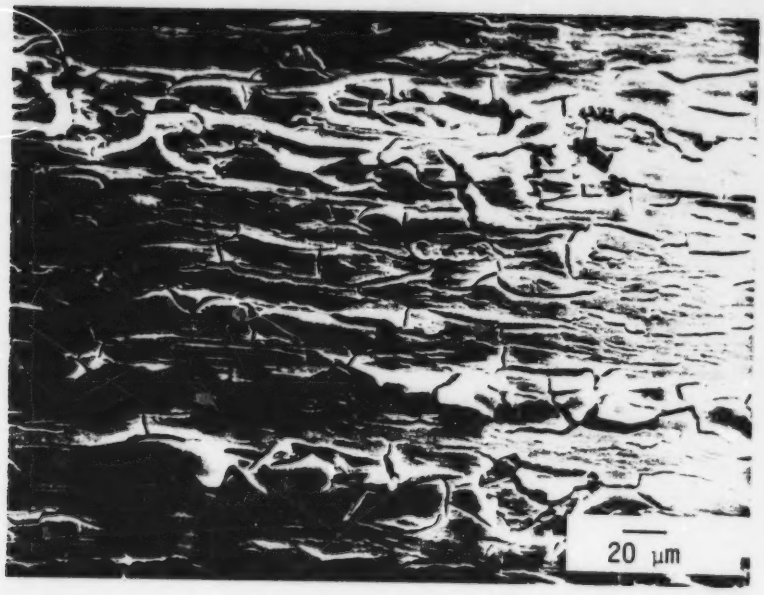

Figure 65.

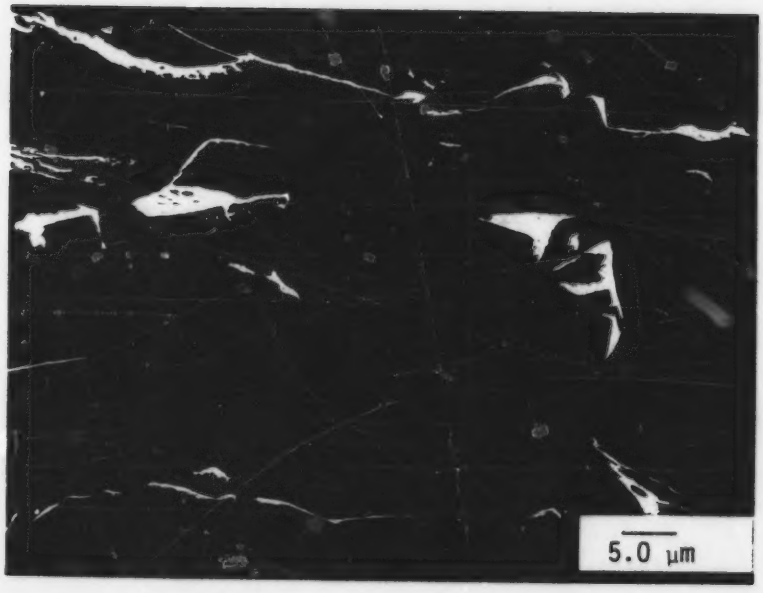

Figure 66.

Figures 65 and 66. Scanning electron micrograph of the polished surface of an eastern high volatile bituminous coal sample after etching for 90 seconds in chromic acid but beofre surface replication has been performed.

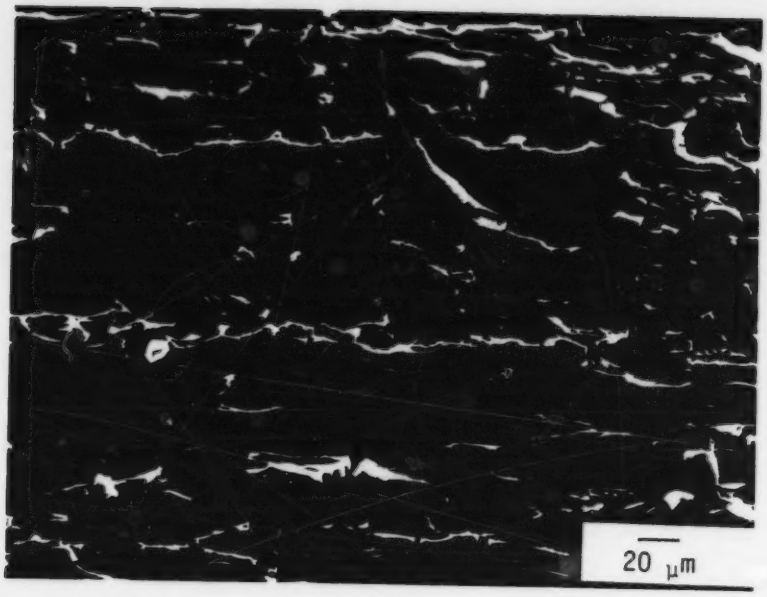

Figure 67.

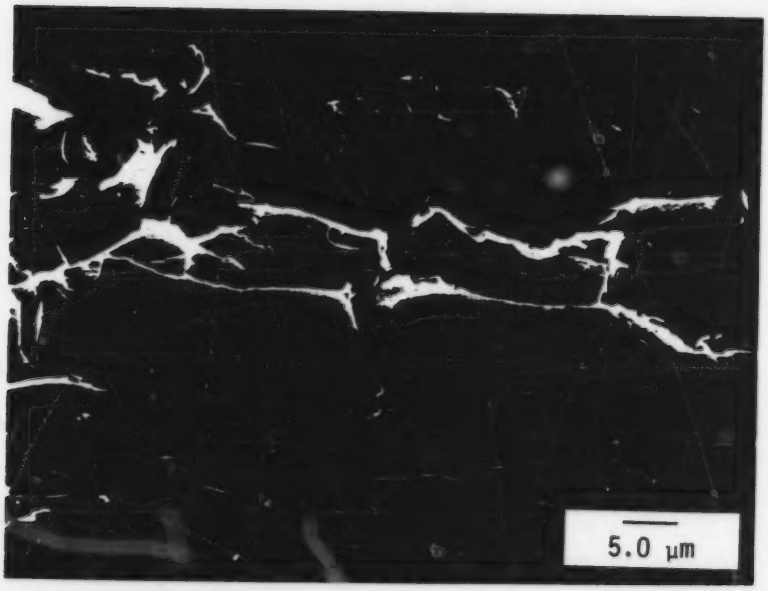

Figure 68.

Figures 67 and 68. Scanning electron micrographs of the coal sample shown in Figures 65 and 66 after the replication process. It is evident that the damage caused by chromic acid etching allows the replication process to remove large amounts of the coal surface.

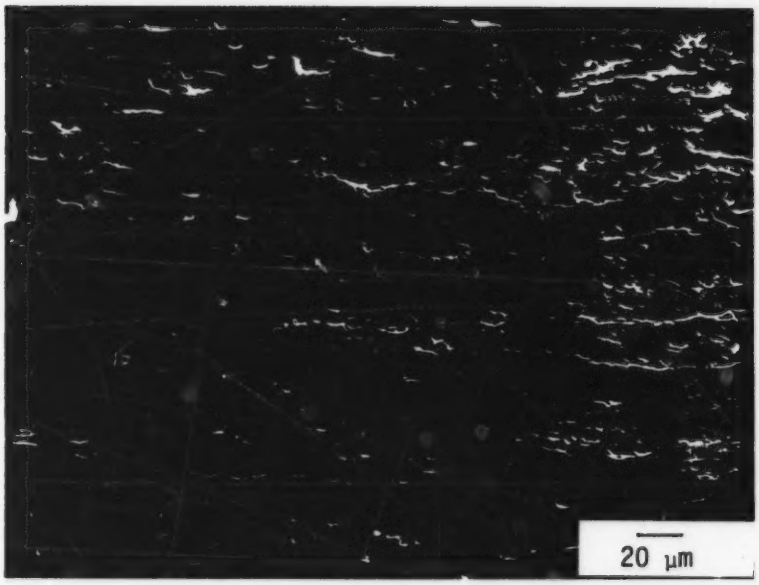

Figure 69. Scanning electron micrographs of an eastern high volatile bituminous coal that has been plasma etched for 60 seconds. It is evident that the etching produced sufficient relief for replication but little or no damage.

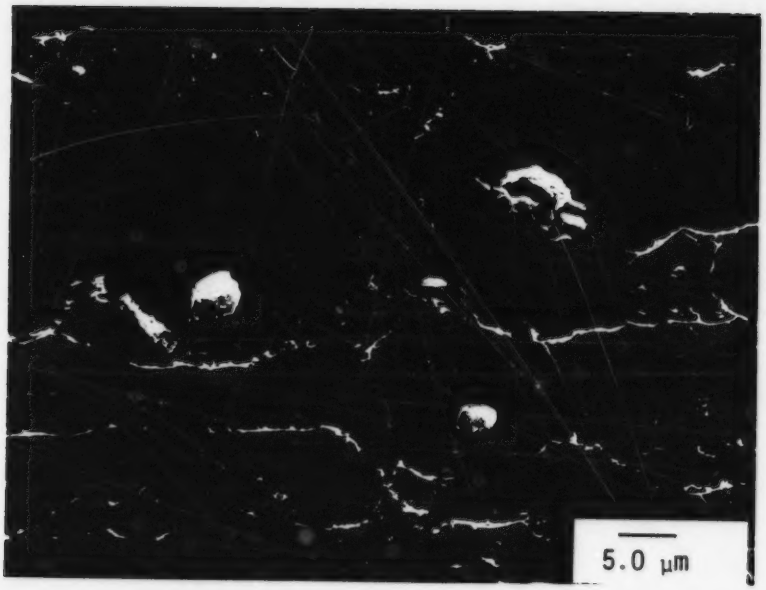

Figure 70. Scanning electron micrograph of an eastern high volatile bituminous coal that has been plasma etched for 5.5 hours illustrating cavities surrounding mineral particles. This suggests that during long periods of plasma etching mineral particles may overheat and gasify coal.

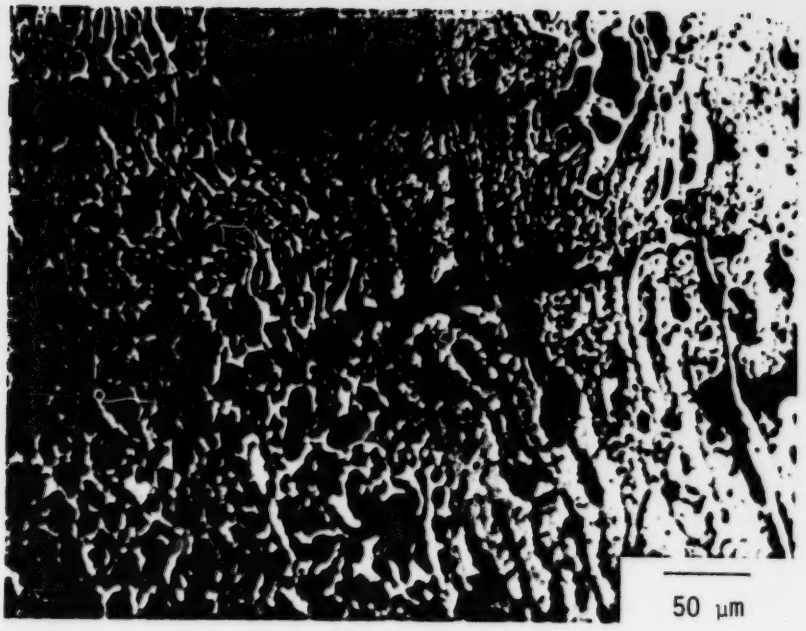

Figure 71.

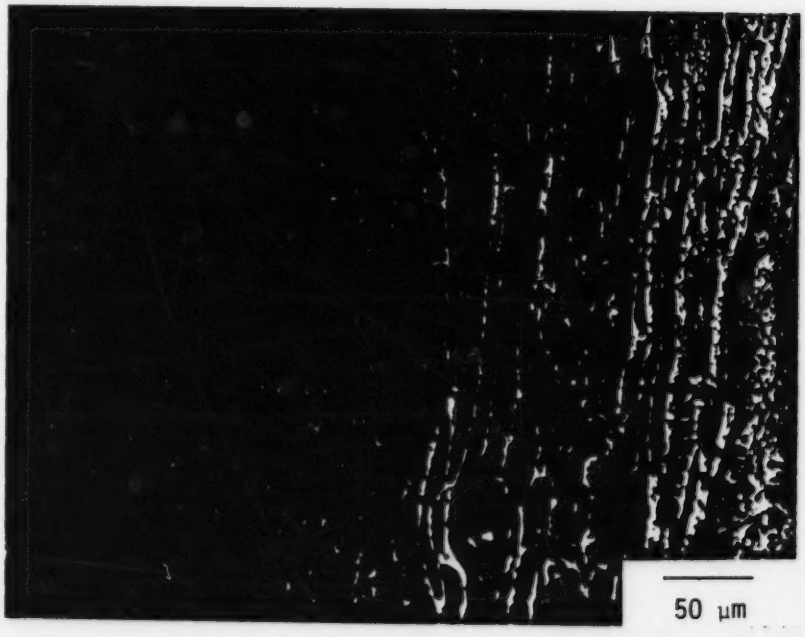

Figure 72.

Figures 71 and 72. Optical micrographs of the selected areas of a western medium volatile bituminous coal prior to replication.

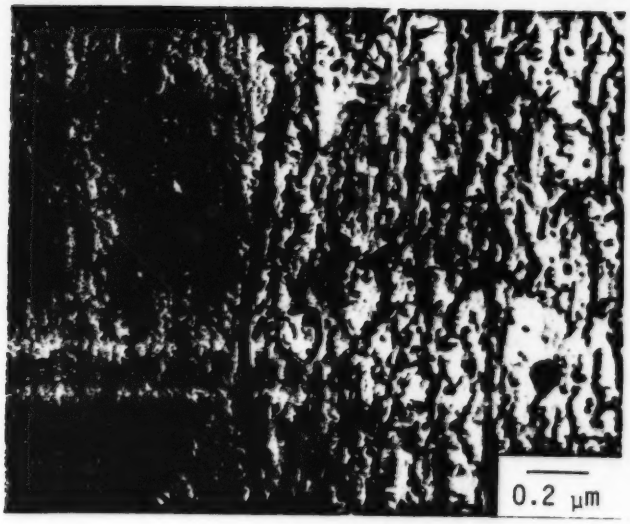

Figure 73.

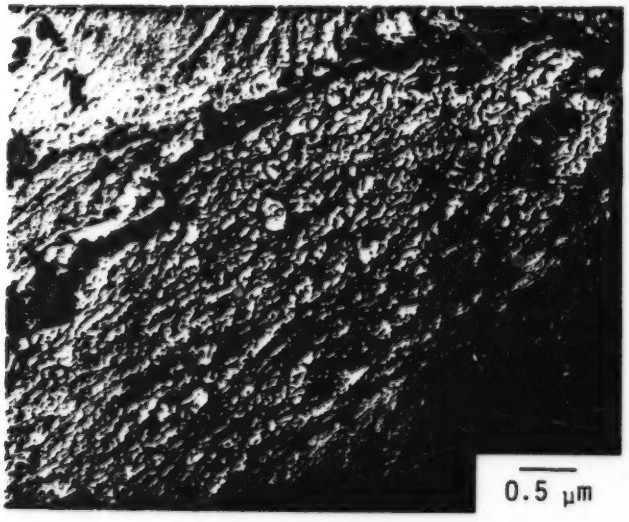

Figure 74.

Figures 73 and 74. Transmission electron micrographs of the replicas obtained from the area of the western medium volatile bituminous coal shown in Figure 71.

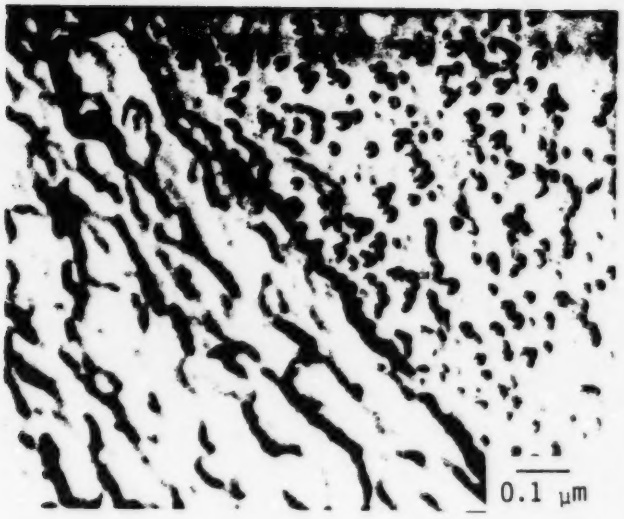

Figure 75.

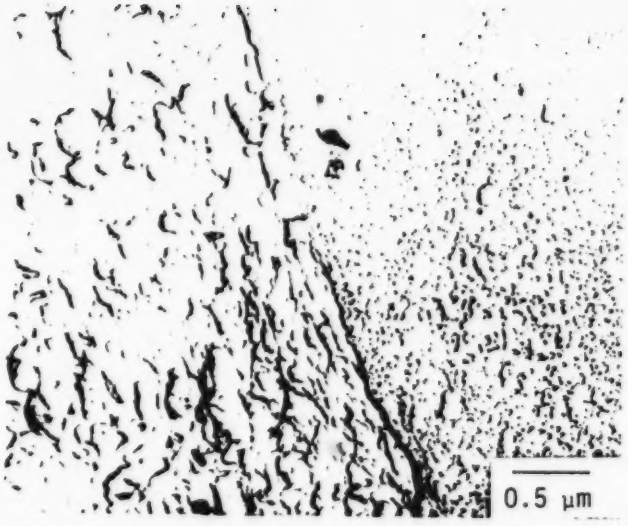

Figure 76.

Figures 75 and 76. Transmission electron micrographs of the replicas obtained from the area of the western medium volatile bituminous coal shown in Figure 72.

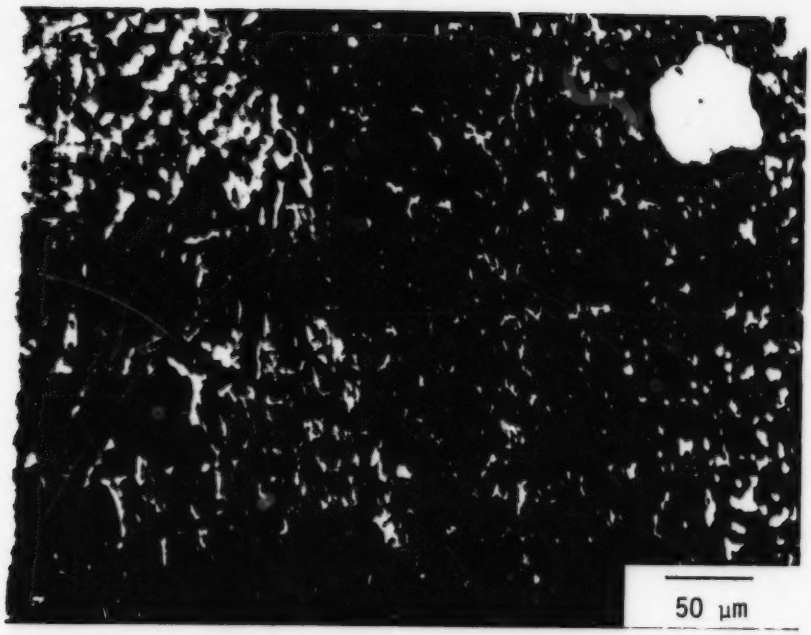

Figure 77. Optical micrograph (reflected light) of the surface of a western low volatile bituminous coal. The dark area contains mineral matter embedded in vitrinite. The lighter area is either fusinite or semifusinite.

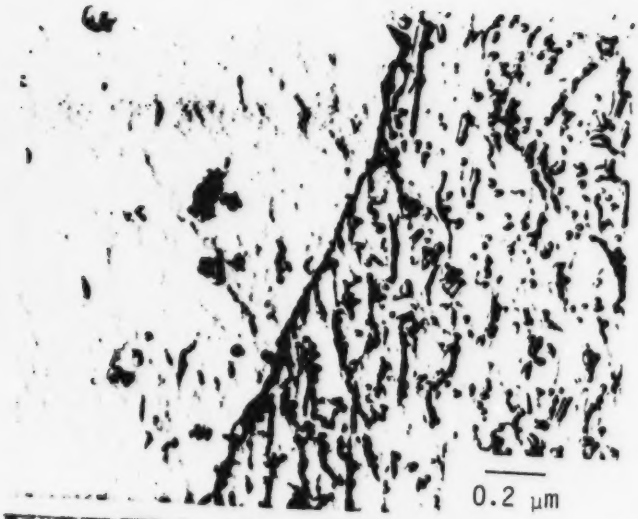

Figure 78.

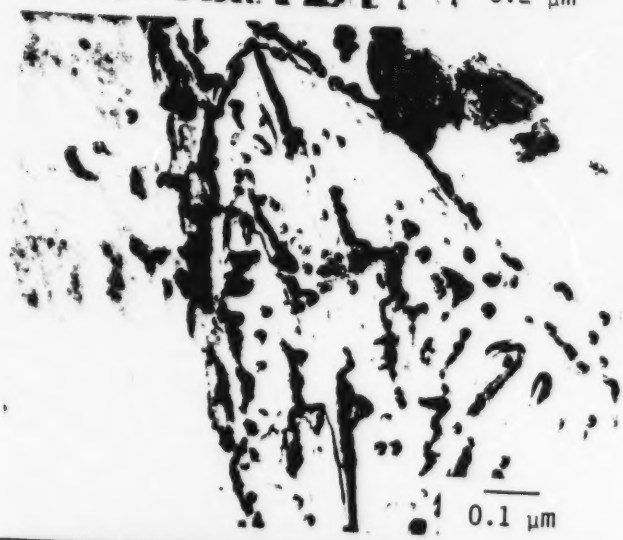

Figure 79.

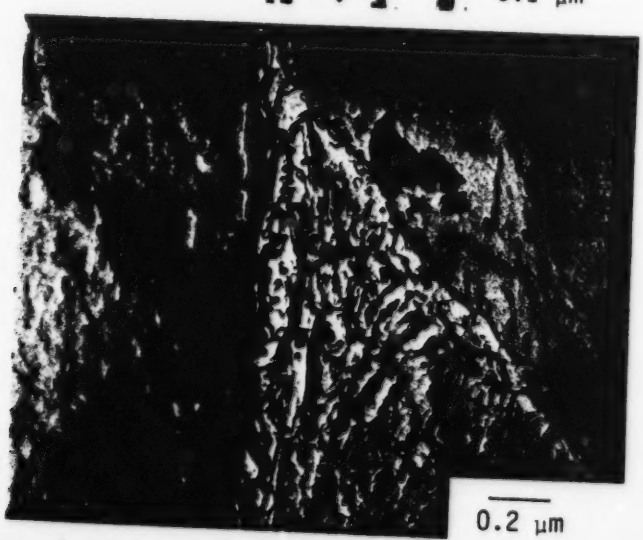

Figure 80.

Figures 78,79 and 80. Transmission electron micrographs of replicas obtained from the semi-fusinite/fusinite area of the western low volatile bituminous coal as indicated in Figure 77.

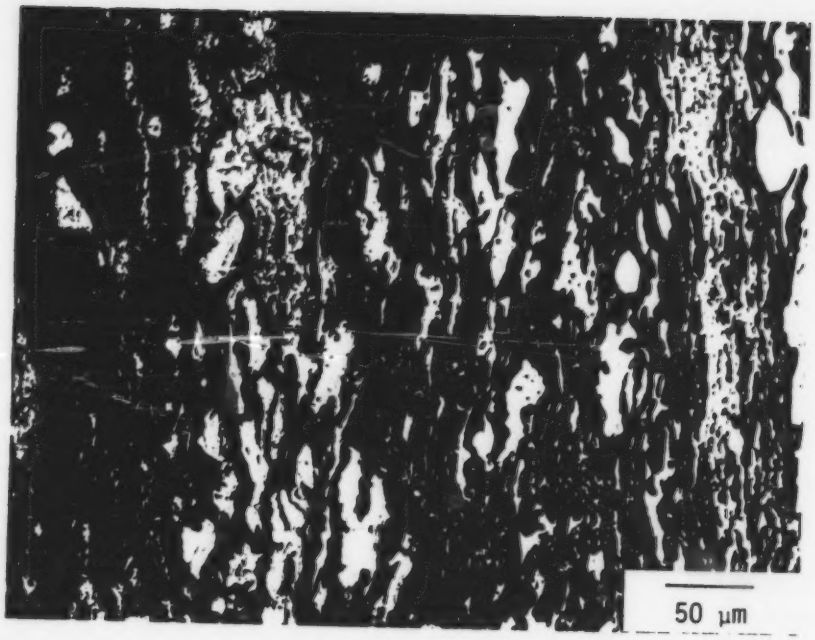

Figure 81. Optical micrograph (reflected light) of an eastern high volatile bituminous coal. The area illustrated in the micrograph is comprised of the macerals semi-fusimite/fusimite, vitrinite and exinite.

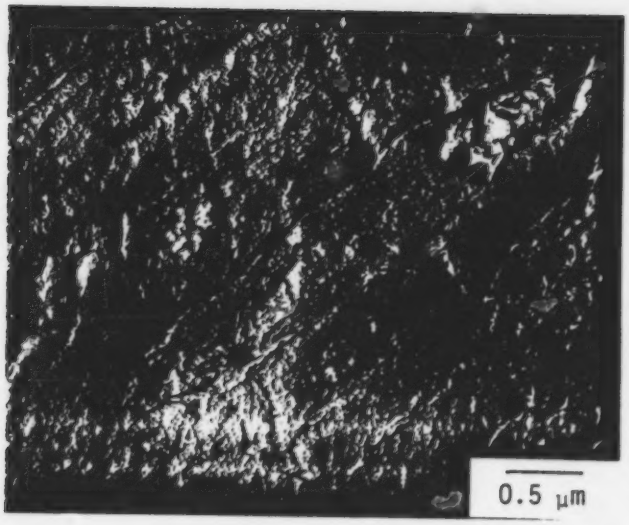

Figure 82.

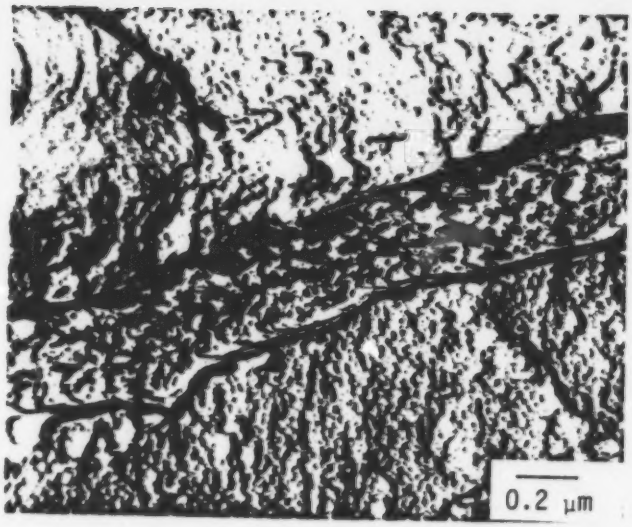

Figure 83.

Figures 82 and 83. Transmission electron micrographs of replicas obtained from the area of the eastern high volatile bituminous coal illustrated in Figure 81.

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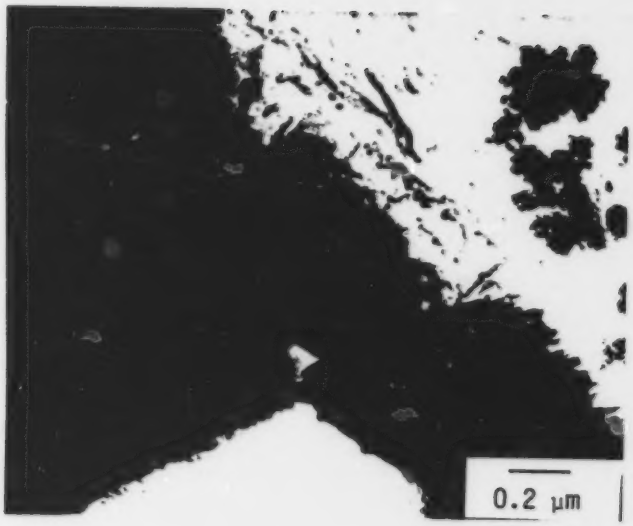

Figure 84. Transmission electron micrograph of a replica of a western low volatile bituminous coal. The micrograph illustrates a piece of coal which has been removed from the sample surface by the replication process. A portion of the coal can be seen to contain what may be coal pores which could result in the dimpled effect on the replica.